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STUDIES OF THE GALACTIC CENTER
I. THE PROGRAM FOR MILKY WAY VARIABLE STARS

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Ever since the study of the space distribution of globular clusters indicated the eccentric position of the solar system in the Galaxy, I have desired to investigate in detail those distant regions in the southern Milky Way where the center of the galactic system appears to be. The usual statistical methods of elucidating galactic structure from rather indiscriminate counts of stars and from measures of motions in the solar neighborhood seem to be too limited—wholly inadequate, in fact, for analysis of regions some twenty thousand to a hundred thousand light years distant. The so-called Kapteyn universe, for instance, is deduced without regard to local clustering, and it combines the data from all galactic longitudes; many earlier attempts to outline the system did not even allow for differences in galactic latitude. The Milky Way system is obviously a conglomerate of single stars, groups of stars, clusters and great star clouds, seriously obscured in certain regions by nebulosity. A direct attack on the problem of the distances of the individual stars in the Milky Way, of the individual nebulae, and of stellar groups, by methods that reach far and give unambiguous results, appears to be the most satisfactory way of working out the details of galactic dimensions and structure, and in particular of determining the nature of the central regions of the galactic system. The researches undertaken to that end will be reported briefly in a series of notes under the title "Studies of the Galactic Center," but the more extensive details, especially the observations dealing with variable stars and star counts, will be published mainly in the Bulletins or Circulars of the Harvard Observatory.

As a preliminary, it should be recalled that all the known globular clusters, about a hundred in number, form a unified, considerably flattened system of still higher order, symmetrical with respect to the galactic plane. Their distances range from fifteen thousand to about two hundred thousand light years, and the greatest diameter of the system, in the

plane of the Galaxy, is between two hundred thousand and three hundred thousand light years. The center of the Galaxy is in the direction of galactic latitude 0°, galactic longitude 327°, and it is so remote that a very asymmetrical apparent distribution is imposed on the globular clusters, which thus appear concentrated in Scorpio, Sagittarius, and the surrounding constellations. Also there appears to be a decided concentration of other remote and highly luminous objects in this same region of the sky, probably the result of the great depth of the Galaxy in the direction of the center, rather than of a real clustering of such objects around the center.

Since the globular clusters are probably good indicators of the form of the Galaxy, of which they are a part, we conclude somewhat tentatively that galactic objects lie in an irregularly circular and much flattened system—a discoidal affair populated by probably not less than 10^{11} stars. Its dimensions may be greater or less than those of the surrounding and concentric system of globular clusters. It is our problem to discover the extent of the Galaxy by direct measurement, instead of continuing to base our estimates largely on the distribution of the globular clusters.

Increasing knowledge of the absolute luminosity of variable stars increases also their usefulness in measuring distances, whether inside the Galaxy, or outside, in globular clusters, Magellanic clouds and extra-galactic nebulae. It now appears that typical Cepheids, cluster type variables, long period variables and to a more limited extent novae and eclipsing binaries, can all be used in the work on galactic dimensions. Ultimately we may use also the planetary nebulae, the open clusters, peculiar types of variables, and stars of extraordinary spectrum and color in this work; and certainly the integrated magnitudes and angular dimensions of globular clusters and extra-galactic nebulae are among the most potent measuring tools, though they are only indirectly used in the present study of galactic structure.

In order to provide material for the general study of faint variable stars as bearing on the Milky Way problem, an extensive observing program was inagurated about five years ago at the Harvard Observatory. The remainder of this note is given to describing the project and reporting some of the preliminary general results.

Variable Star Fields.—The distribution of the centers of the 240 Harvard Milky Way variable star fields is indicated in galactic coördinates in figure 1. It is seen that three parallel series of overlapping fields extend over the whole length of the Milky Way. The separation of the centers is governed by the focal lengths of the principal telescopes used for the study in the northern and southern hemispheres. Some of the cameras with especially short focus and large covering capacity extend at one time over the whole of four to eight fields.

The 182 regular fields along the central belt of the Milky Way will contain, of course, a great majority of the discoverable variables and of all other stars of the Milky Way fainter than the twelfth magnitude; but to make the study representative of the whole sky, without actually covering in detail the relatively barren expanses in high galactic latitude, we are supplementing the comprehensive work near the galactic equator with a number of systematically distributed fields in higher galactic latitudes; there are also several supplementary fields in the neighborhood of the center of the Galaxy, and a few elsewhere along the Milky Way.

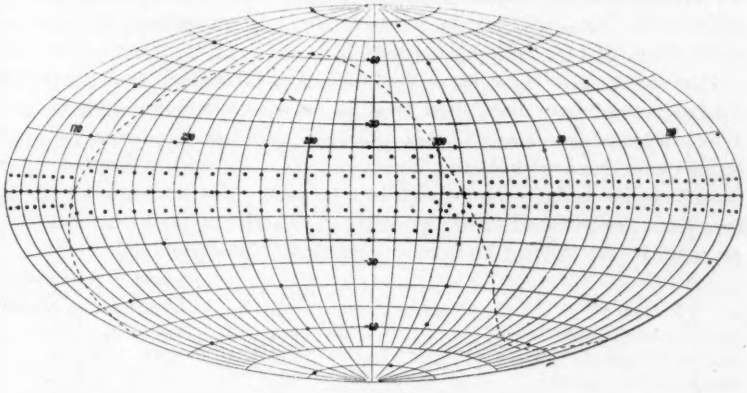

FIGURE 1

Distribution in galactic coördinates of centers of Milky Way variable star fields. Celestial equator is shown by broken line.

For at least three-fourths of the fields the stars down to magnitude 16.5 will be photographed; in special regions near the galactic center and elsewhere, the survey will later be taken to the nineteenth and twentieth magnitudes. The number of plates accumulated, in the ten or fifteen years during which this observing program will be maintained, will naturally depend on the character of the faint variable stars discovered. It will aim to be sufficient for determinations of the periods, ranges and light curves of all the periodic variables discovered. For most of the brighter and many of the fainter variables the secular or long period changes in the periods and light curves can also be found by using plates already available in the Harvard collection. There are, in fact, approximately sixty thousand plates made before the program was started that will be suitable for this research on Milky Way variables. Most of them, to be sure, show stars only to the twelfth magnitude, and are therefore not very effective in the work on the faintest variables.

In the present problem the uncertainty of photographic magnitude

standards and the infrequency of reliable comparison sequences of faint stars will again be the most serious hindrance to accurate work on distant stars. It is probable that the absolute magnitudes of most of the fainter variable stars will soon be known with greater accuracy than their apparent magnitudes. Photographic magnitudes have been measured at Harvard for more than eight hundred sequences, well distributed over the sky. It is planned to carry on actively the improvement and extension of the existing magnitude standards in the immediate future; for certainly the problem of stellar distances has become a question of photometry. The concentration of the Henry Draper Extension to Milky Way regions has been largely influenced by the need of faint spectra for both the photometric work and the study of variable stars in the Milky Way.

The Photographic Cameras.—The following tabulation shows the instruments that have been used thus far in the systematic work on the Milky Way fields. The *AC*, *AM*, *AX*, *AY*, *RH* and *RB* series are only in part concerned with Milky Way variables. As used at present their lower magnitude limits range from 11.5 to 14.5. The *AM* and *AY* series have been discontinued for the present. The series marked with asterisks are made at the Boyden Station, at Arequipa or Bloemfontein.

INSTRUMENT	SERIES	FOCAL LENGTH (INCHES)	WORKING APERTURE (INCHES)	DIAMETER OF WORKING FIELD (DEGREES)
Bruce 24-inch doublet	*A**	135	24	4.4
Metcalf 16-inch doublet	*MC*	83	16	5
Metcalf 12-inch doublet	*MA*	87	12	5
Metcalf 10-inch triplet	*MF**	49	10	8
Draper 8-inch doublet	*I*	50	8	8
Cooke 4-inch triplet	*MD*	42	4	10
Ross-Fecker 3-inch	*RH*	21	3	15
Ross-Fecker 3-inch	*RB**	21	3	15
Zeiss-Tessar 3-inch	*AX**	13	2	25
Zeiss-Tessar 3-inch	*AY*	13	2	25
Cooke 1-inch	*AC*	13	1	25
Cooke 1-inch	*AM**	13	1	25

Number of Recorded Variable Stars.—The total number of variable stars listed in Prager's 1928 catalogue (which does not include those of the Magellanic Clouds, globular clusters, or spiral nebulae) is 3026. Of these, approximately fifty-five per cent lie in the Milky Way regions. Several hundred additional variables have been discovered within the present year at Harvard and elsewhere. Since this observing program began the numbers of new variable stars found by various workers on Harvard plates are approximately as follows:

S. I. Bailey	58	J. S. Paraskevopoulos	18
C. D. Boyd	180	H. H. Rehnborg	40
A. J. Cannon	90	H. Shapley	34
B. P. Gerasimovič	33	H. H. Swope	385
M. A. Gill	50	W. F. H. Waterfield	25

W. J. Luyten	87	I. E. Woods	250
J. Mohr	60	Miscellaneous	50
		Total	1360

At least two-thirds of these variables are fainter than the fourteenth magnitude. Therefore in general their distances exceed thirty thousand light years.

The Central Region.—Although the whole circuit of the Milky Way is covered in the observing program, it is obvious that more attention should be given to the region in the direction of the galactic center, not only because of our curiosity concerning that part of the universe, but because of the much greater star density—apparent and possibly real. The region between latitudes $+20°$ and $-20°$, longitudes $290°$ and $350°$, has been laid out for special study (Fig. 2). This is a region rich in discovered

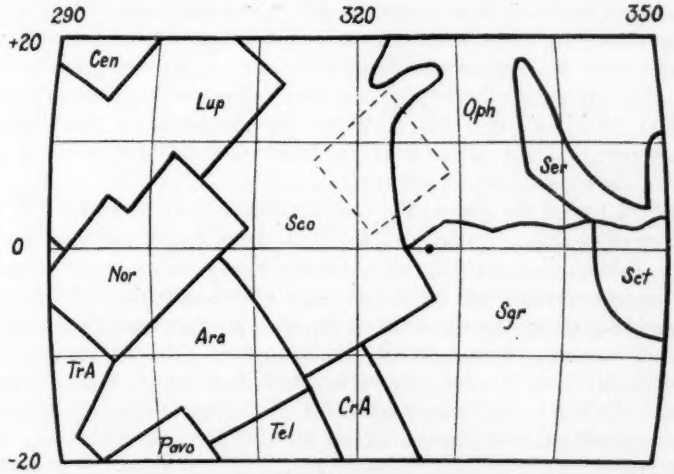

FIGURE 2

Map of the region of special study around the galactic center. The broken-lined quadrilateral is MWF 185, a field rich in variable stars, which is discussed in the following note of the series. The point at 327°, 0°, is the galactic center indicated by globular clusters.

and undiscovered variable stars, and some of it is affected by heavy obscuring nebulosity, which may seriously hamper our investigation of the region. As will appear from subsequent notes, we are studying not only the variables in this region of nearly $60 \times 40 = 2400$ square degrees, but also the number and distribution of nebulae, clusters and stars of various types. The following note will give a preliminary idea of the distance of the main body of stars near the galactic center and indicate the success with which the investigation of variable stars may reveal important details of the structure of the Galaxy.

STUDIES OF THE GALACTIC CENTER
II. PRELIMINARY INDICATION OF A MASSIVE GALACTIC NUCLEUS

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The galactic variable star field designated as MWF 185, which is centered on right ascension $16^h\ 53^m$, declination $-28°.2$, covers effectively an area of seventy square degrees (MF plates) on the north side of the Milky Way in Ophiuchus and Scorpio. At its nearest point it is only five degrees from the accepted direction to the center of the Milky Way. The region proves to be uncommonly rich in variable stars. Miss Leavitt found twenty-six many years ago, all of them brighter than the fourteenth magnitude.[1] Dr. Luyten and Miss Woods have found thirteen and twenty-four, respectively, in this region,[2] and nine others are known from various sources. Thus a total of seventy-two variables was on record before the systematic study of the field was undertaken by Miss Swope a year ago.[3] The number now known is about 450.

Only a few of the previously known variable stars in MWF 185 had been studied sufficiently to give the type, period and magnitude; but the types have now been determined for approximately 165, and for seventy of them the periods and light curves have also been derived. It is of interest that the systematic work on the Harvard plates first preferentially yielded variables of long period and large range; further examination brought out many cluster type variables of small range, their discovery being facilitated by the use of a binocular microscope of considerable power and a special series of plates made on the globular cluster N. G. C. 6266 with the Bruce 24-inch telescope in Peru. The examination of further plates will probably bring out an increasing number of eclipsing stars. The variables were found in general by the method of using superposed positives and negatives.[4]

The magnitudes of the variable stars which have now been measured are based on Sequence No. 35 of Kapteyn's special list. It is unfortunately necessary to consider the magnitudes provisional, and to keep in mind that a systematic error of some tenths of a magnitude is still possible, though improbable; the uncertainty is in zero point, rather than in magnitude scale, since the observed ranges of the numerous Cepheid variables afford a fair check on scale.

For twenty-six cluster type variables the periods have been determined and show the distribution with respect to median magnitude given in the second column of the accompanying table. The periods range from $0^d.2825$

to $0^d.707$, and there is little doubt that almost without exception these stars are typical cluster type variables. For fifty-two other variables of this type the observations are as yet insufficient to give definite periods, but they suffice to show without doubt the nature of the variation and to give the maximum, minimum and median magnitudes. Their distribution is shown in column 3 of the table. The totals are twice plotted in the diagram, for intervals of one and two-tenths of a magnitude.

FREQUENCY OF CLUSTER TYPE VARIABLES IN MWF 185

PHOTOGRAPHIC MEDIAN MAGNITUDE	NUMBER OF VARIABLES PERIOD DETERMINED	PERIOD UNDETERMINED	TOTAL	PHOTOGRAPHIC MEDIAN MAGNITUDE	NUMBER OF VARIABLES PERIOD DETERMINED	PERIOD UNDETERMINED	TOTAL
14.0	0	0	0	15.2	0	2	2
14.1	0	1	1	15.3	1	3	4
14.2	0	0	0	15.4	1	4	5
14.3	1	1	2	15.5	4	4	8
14.4	1	4	5	15.6	1	5	6
14.5	0	1	1	15.7	5	6	11
14.6	0	1	1	15.8	3	4	7
14.7	0	1	1	15.9	1	4	5
14.8	0	3	3	16.0	2	3	5
14.9	0	0	0	16.1	4	1	5
15.0	0	0	0	16.2	1	1	2
15.1	1	3	4				

The frequency distribution of the median magnitudes is remarkable. None of the variables is brighter than the fourteenth magnitude. For fourteen of the seventy-eight stars the magnitudes are scattered from 14.1 to 14.8. For the other sixty-four variables the magnitudes are all between 15.1 and 16.2, inclusive, with a maximum frequency at 15.7 and a fairly normal distribution about the mean value of 15.66. The standard deviation of one observation is 0.29, and that of the mean is 0.04.

It appears certain, therefore, since the absolute luminosities of cluster type variables have little dispersion about the mean absolute magnitude zero, that we are dealing here with a definitely bounded stellar system, and that the dispersion in the observed apparent magnitudes of the sixty-four cluster type variables is due to errors of measurement and to the distribution of the variables throughout the depths of the star cloud in which they are situated. The fourteen brighter variables lie on this side of the star cloud, with distances from 21,000 to 30,000 light years.

We can easily estimate the degree of dispersion in the magnitudes due to the different distances of the variables in the line of sight, assuming for the purpose of computation that observational errors are negligible and that the median absolute magnitudes are actually identical. Or from the dispersion we may estimate the dimensions of the cloud. If magnitude 16.2 refers to variables at the farthest edge of the star cloud and magnitude 15.1 to those at the nearest edge, then the magnitude difference, Δm,

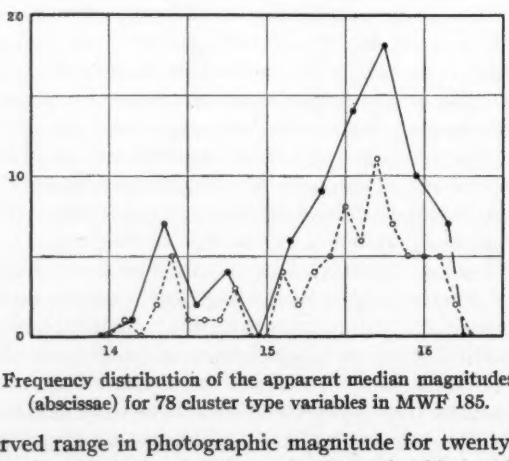
is 1.1, and is equal to 2.5 ($\log L_n - \log L_f$), where the subscripts n and f refer to the nearest and farthest edges of the cloud. Since the light, L, varies inversely as the square of the distance, d,

$$5 \log d_f/d_n = 1.1$$

and

$$d_f/d_n = 1.66$$

The radius of the cloud is therefore approximately equal to one-third the distance of the center from the earth. If the cloud is spheroidal, the angular diameter is nearly 40°. Such dimensions are reasonable. The diameter of the nebulosity-bordered star cloud in which MWF 185 is situated, is 12°; the whole assemblage of star clouds in this region extends over an area 30° by 70°. It is probable, however, that unrecognized superposed variables, as well as observational errors and incompleteness, contribute something to the dispersion of median magnitudes and that only a part of the observed dispersion is to be accounted for by the extent of the cloud in the line of sight. With more and better observations on variable stars we shall be able to get fairly accurate measurements of the size of the cloud.



Frequency distribution of the apparent median magnitudes (abscissae) for 78 cluster type variables in MWF 185.

The observed range in photographic magnitude for twenty-five cluster type variables for which the periods can be determined is 1.14 in the mean; for the remainder of the stars, the average range is three-tenths of a magnitude smaller. Probably this difference is due in part to a selective factor—the difficulty of determining periods for the shorter ranges—and in part to the effect of background stars in making the observed minimum magnitudes too bright. The correction for the background is not simple, either in individual cases or for the mean; but it seems best to adopt the mean value $m = 15.8$ as the apparent median magnitude for the sixty-four

stars which we consider members of the cloud, instead of taking the observed mean value of 15.66 ± 0.04.

If we take 0.0 as the absolute median magnitude of cluster type Cepheids, the distance to the center of the region under discussion is given by

$$\log d = 1 + 0.2\,(m - M) = 4.16$$
$$d = 14{,}400 \text{ parsecs}$$

We estimate that the chances are even, or better than even, that the true mean value of $m - M$ for the whole group lies somewhere between 15.6 and 16.0. The corresponding probable error in the distances is about ten per cent. A probable error of twenty per cent would permit the quite unnecessarily wide "even chance" magnitude limits of 15.3 to 16.2 for the true mean.

The distance of 14.4 kiloparsecs (47,000 light years) is the same, within admitted errors, as the distance to the center of the higher system of globular clusters, which has also been accepted, at least tentatively, as the center of the galactic system. It thus appears that in exploring the rich star cloud in Scorpio and Ophiuchus, as shown on MWF 185, we have been measuring a portion of the central nucleus of the galactic system.

Lanes of obscuring nebulosity cut off the star cloud on MWF 185 from the richer regions across the galactic equator in Sagittarius and adjoining constellations; but there can be little doubt that behind the dark nebulosity the star clouds are dense and continuous. A massive galactic nucleus is indicated, at a distance of nearly fifty thousand light years. Its diameter perpendicular to the galactic equator is some thirty degrees, corresponding to 25,000 light years, but its extent along the Milky Way and in the line of sight is less certain. In no other part is the Milky Way so broad or rich as in this central region.

It is premature to dwell on the possible analogy of the galactic nucleus with the central portions of certain spiral and spindle nebulae. To be sure of our grounds it will be necessary first to cross the galactic equator, with our detailed analysis of faint variables, into the Scorpio-Sagittarius star clouds; it will also be necessary to consider if our apparent magnitudes have been dimmed by light-scattering nebulosity, even in the apparently clear regions such as MWF 185. This possibility of light obstruction is probably not very serious, however; the distances derived for the great star clouds and independently for the center of the Galaxy through the aid of globular clusters are very similar, and also in these star fields there are numerous extra-galactic nebulae, indicating the high transparency of the region. The distribution of the extra-galactic nebulae in the direction of the galactic center will be exhibited in a later paper. The next note will present further evidence of the existence of the galactic nucleus, basing it on variable stars of another kind.

[1] Leavitt, *Harv. Obs. Circ.* 90, 1904.
[2] Luyten, *Harv. Obs. Bul.* 852, 1928; Woods, *Ibid.*, 834, 1926.
[3] Swope, *Harv. Obs. Bul.* 857, 1928; approximately one hundred and sixty of the variables found by Miss Swope have not yet been published.
[4] *Harv. Obs. Circ.* 79, 1904.

THE DETERMINATION OF ABSOLUTE-MAGNITUDE DISPERSION WITH APPLICATION TO GIANT M STARS

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The problem of finding the distribution according to absolute magnitudes of a group of stars is one of considerable importance. Except for the case in which all the stars in the group are at approximately the same distance, the problem can usually be solved only by making certain assumptions as to the nature of the distribution function, either of the absolute magnitudes, or of the accidental and systematic errors in the measured absolute magnitudes. If we may assume that the distribution of the absolute magnitudes in the group is that corresponding to a normal error distribution, or that the errors in the measured absolute magnitudes have this distribution, the problem is definite and can be solved by comparing the distribution of angular velocities with that of the radial velocities. A solution for the case of the second alternative is published in *Mount Wilson Contributions*, No. 327,[1] in connection with the determination of the errors in the spectroscopic absolute magnitudes of giant M stars; but since the modification of the formulas required for the case of the first alternative was only parenthetically referred to, the direct solution of the problem will be given here. It will also be shown that Gyllenberg's solution of the problem can be derived in the same way.

We assume that the absolute magnitudes of a group of stars are distributed according to a normal error curve around a mean value $\bar{M}$ and with a dispersion q. The individual true absolute magnitudes are denoted by M. The frequency function of the absolute magnitudes is then

$$F(M)dM = \frac{1}{\sqrt{2\pi}q} e^{-\frac{(M-\bar{M})^2}{2q^2}} dM. \qquad (1)$$

Let τ be any component of the proper motion of a star, corrected for the parallactic motion, and m the apparent magnitude. The linear velocity T in km./sec. in the direction of τ is then

$$T = 10k\tau 10^{0.2(m-M)} = 10k\tau' 10^{-0.2M} \qquad (2)$$

where $k = 4.738$ km. year/sec., and τ' is the reduced proper motion defined by

$$\tau' = \tau\, 10^{0.2m}.$$

Before forming any means of the T's we must remember that τ' is correlated to M. We will assume, however, that T is not correlated to M. This assumption can be made if the spread in absolute magnitude is not too large. Multiply equation (2) by $10^{0.2M}$ and form the mean without regard to signs. The mean T thus found is statistically comparable with θ, the average peculiar radial velocity.
Thus

$$\overline{10^{0.2M}}\,\theta = 10k\tau'_m$$

where τ'_m is the mean τ' formed without regard to the signs. Denoting $M - \overline{M}$ by Δ, we have

$$10^{0.2\overline{M}}\,\overline{10^{0.2\Delta}}\,\theta = 10k\tau'_m \qquad (3)$$

Further

$$\overline{10^{0.2\Delta}} = A = \frac{1}{\sqrt{2\pi}\,q}\int_{-\infty}^{+\infty} 10^{0.2\Delta}\, e^{-\frac{\Delta^2}{2q^2}}\, d\Delta. \qquad (4)$$

By evaluating the integral, we find the following relation between A and q (the logarithms here and in the following are all to the base ten)

$$q^2 = 50 \text{ Mod} \log A = 21.71 \log A. \qquad (5)$$

Hence

$$\overline{M} = 5 + 5 \log \frac{k\tau'_m}{A\theta}. \qquad (6)$$

To determine A and q we must have recourse to moments of higher order of the velocities. Forming the mean of the squares, we find

$$10^{0.4\overline{M}}\,\overline{10^{0.4\Delta}}\,\overline{V^2} = 100k^2\overline{\tau'^2} \qquad (7)$$

The symbol $\overline{V^2}$ here indicates the mean of the squares of the peculiar radial velocities. But

$$\overline{10^{0.4\Delta}} = \frac{1}{\sqrt{2\pi}\,q}\int_{-\infty}^{+\infty} 10^{0.4\Delta}\, e^{-\frac{\Delta^2}{2q^2}}\, d\Delta = B.$$

Evaluating the integral, we find

$$B = e^{0.08q^2/\text{Mod}^2} = A^4. \qquad (8)$$

Equation (7) thus becomes

$$10^{0.4\overline{M}}A^4\overline{V^2} = 100k^2\overline{\tau'^2},$$

and combining with (3),

$$A^2 = \frac{\overline{\tau'^2}\,\theta^2}{\tau_m'^2\overline{V^2}}. \qquad (9)$$

Equations (9), (5), and (6) now give the mean $\overline{M}$ and the dispersion q.

Another formula has been derived by Gyllenberg.[2] He finds the expression

$$q^2 = \frac{25}{4}\,\mathrm{Mod}\left[\log\left(\frac{8}{3}E + 1\right) - \log\left(\frac{8}{3}H + 1\right)\right]. \qquad (10)$$

The numerical coefficient is equal to 2.7143, and E and H are the values for the "excess" in the distribution of the proper motion components and radial velocities, respectively. Remembering the definition of "excess" as used by Gyllenberg, we have, in the present notation

$$E = \frac{1}{8}\left(\frac{\overline{\tau'^4}}{\overline{\tau'^2}^2} - 3\right); \quad H = \frac{1}{8}\left(\frac{\overline{V^4}}{\overline{V^2}^2} - 3\right).$$

Equation (10) is thus equivalent to

$$q^2 = \frac{25}{4}\,\mathrm{Mod}\log\frac{\overline{\tau'^4}\;\overline{V^2}^2}{\overline{\tau'^2}^2\;\overline{V^4}}. \qquad (11)$$

This formula is analogous to equations (5) and (9), and would have been found had we used the moments of fourth and second orders, instead of those of the second and first, and taken into account the relation

$$\overline{10^{0.8\Delta}} = A^{16}.$$

An expression equivalent to equation (9) had also been derived by Gyllenberg in the same paper.

The introduction of the excess may, however, be misleading. If with Charlier we define the excess as three times the coefficient of the fourth derivative of the error function, the relation between the absolute-magnitude dispersion and the excess in the proper motion and in the radial-velocity distributions cannot be uniquely expressed. If we determine the excess from the moments of second and first order, the latter with disregard of signs, the proper expression is

$$q^2 = 50\,\mathrm{Mod}\log\frac{1 - \frac{H}{3}}{1 - \frac{E}{3}}.$$

This formula is equivalent to equations (5) and (9), but is concordant with (10) only for small values of H and E. Equations (5) and (9) are the best for numerical purposes, since we do not have to form means of quantities raised to the fourth power, which obviously are rather uncertain.

When the radial velocities are not known, we can, in most cases, replace with sufficient accuracy,

$$\theta^2 : \overline{V^2} \text{ by } 2 : \pi = 0.637.$$

The solution of the problem of finding the systematic correction and the mean error in the spectroscopic absolute magnitudes of a group of stars is now obvious. The reduced τ-component must be replaced by

$$\tau'' = 10\tau\, 10^{0.2(m-M_1)} = \frac{\tau}{\pi_1},$$

where π_1 and M_1 are the spectroscopic parallax and the spectroscopic absolute magnitude, respectively. The systematic correction S is then defined by the equation

$$S = 5 \log \frac{k\tau''_m}{A\theta}. \qquad (12)$$

This formula is identical with equation (8) in my former study.[1]

The mean error q in an individual absolute magnitude is now given by the formulas

$$q^2 = 21.71 \log A; \quad A^2 = \frac{\overline{\tau''^2}\ \theta^2}{\tau''^2_m\ \overline{V^2}}. \qquad (13)$$

When the proper motions are small, they must be corrected for the systematic effect of the accidental errors as explained in *Contribution* No. 327.[1] The effect of systematic errors in the proper motions is in this case, however, rather serious.

In a recent issue of these PROCEEDINGS[2] Luyten has discussed the frequency of absolute magnitudes of giant M stars as derived from the spectroscopic data of Adams, Joy and Humason.[4] In particular he calls attention to the small dispersion in the spectroscopic absolute magnitudes for stars outside the galactic zone, and concludes that, if we assign a constant absolute magnitude of -0.1 to these stars, the mean error for an individual star is only ± 0.34. This result seems at first to contradict the value of ± 0.66 given in *Contribution* No. 327 for the mean error in the absolute magnitudes of ordinary giant M stars, which are comparable with those outside the galactic zone. But Luyten has evidently overlooked the fact that my determination is based on proper motion and radial velocity data, whereas his is the dispersion in the spectroscopic absolute magnitudes. Even if

these showed no dispersion whatsoever, there might still be a spread due to a lack of correspondence between the true absolute magnitudes and the spectral criteria used.

The method here developed enables us to find how accurate the assumption of a constant absolute magnitude for giant M stars outside the galactic zone really is. I have made such a computation, using the Boss stars in the list of spectroscopic absolute magnitudes brighter than apparent magnitude 6.5, and have grouped the stars in two groups, one in the galactic zone and one outside galactic latitude $b = \pm 20°$. The results are given in the accompanying table. The third and fourth columns give the mean

b	No.	$\overline{M}_s$	q_1	$\overline{M}_o$	q_2	S	q_3	θ km./sec.	$\theta^2:\overline{V}^2$
0 to $\pm 19°$	73	−0.54	0.98	−0.77	1.16	−0.45	1.12	16.9	0.64
± 20 to $\pm 90°$	172	−0.09	0.35	−0.21	0.66	−0.08	0.55	19.0	0.57

of the spectroscopic absolute magnitudes and the corresponding dispersion. These figures are comparable with Luyten's values and agree well with his results. The mean absolute magnitude $\overline{M}$ and the corresponding dispersion q_2 computed with the aid of equations (6), (9), and (5) are next given. The value of q_2 is the mean error of an individual absolute magnitude which is to be expected if we assume that all the stars in the group have the same absolute magnitude $\overline{M}$. If next we assume that the true absolute magnitude is equal to that spectroscopically determined, plus a constant systematic correction, we find this correction S and the mean error q_3 of an individual absolute magnitude to be as in the next two columns. It is this q_3, and not q_1, which is to be compared with q_2 in estimating the gain made by determining the intensities of spectral lines, instead of depending on the galactic latitude and apparent magnitude. The gain is not large and amounts to a reduction in the mean error of 3 and 17 per cent, respectively, in the two zones. The mean error in the absolute magnitude for the galactic stars seems abnormally large, a fact no doubt due to the high proportion of super-giants, whose absolute magnitudes cannot be determined very accurately by the criteria now in use.[1]

The last two columns in the table give the average peculiar radial velocity θ, and the ratio $\theta^2:\overline{V}^2$, which does not differ greatly from the theoretical value 0.637.

[1] *Astroph. J., Chic., Ill.*, **65**, 1927 (108–116).

[2] *Meddelanden från Lunds Astron. Obs., Lund, Sweden*, Ser. II, No. 41a, p. 11, 1928 (Charlier Festskrift).

[3] These PROCEEDINGS, **14**, 1928 (488–491).

[4] *Mt. Wilson Contr.*, No. 319; *Astroph. J., Chic., Ill.*, **64**, 1926 (225–242).

GUDERMANNIAN COMPLEX ANGLES

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It is well known[1] that corresponding to any real positive hyperbolic angle θ (hyperbolic radians) there exists a real positive circular angle β (circular radians) defined by the relations:

$$\sin \beta = \tanh \theta \tag{1}$$
$$\cos \beta = \operatorname{sech} \theta = 1/\cosh \theta \tag{2}$$
$$\tan \beta = \sinh \theta \tag{3}$$
$$\cot \beta = \operatorname{csch} \theta \tag{4}$$
$$\sec \beta = \cosh \theta \tag{5}$$
$$\csc \beta = \coth \theta. \tag{6}$$

This circular angle β is commonly called the "gudermannian" of θ and the relation is expressed by the two well-known real equations:

$$\beta = gd\,\theta \quad \text{real circular radians} \tag{7}$$

and

$$\theta = gd^{-1}\beta \quad \text{real hyperbolic radians} \tag{8}$$

so that the hyperbolic angle θ is the antigudermannian or lambertian of β. Gudermannians of a real θ have been tabulated from[2] $\theta = 0$ to $\theta = 6$.

It is the object of this note to point out, however, that the preceding equations are not limited to real angles; but pertain to complex angles throughout. That is, if $i = \sqrt{-1}$, (9)

$$\beta = \beta_1 + i\beta_2 = gd\,\theta = gd(\theta_1 + i\theta_2) \quad \text{complex cir. radians} \tag{10}$$

and

$$\theta = \theta_1 + i\theta_2 = gd^{-1}\beta = gd^{-1}(\beta_1 + i\beta_2) \quad \text{complex hyp. radians} \tag{11}$$

where β_1 and β_2 are, respectively, real and imaginary components of β; while θ_1 and θ_2 are the corresponding components of θ. Here β_1 is essentially a real circular angle, and θ_1 a real hyperbolic angle; while $i\beta_2$, being an imaginary circular angle, may be regarded as a hyperbolic angle, and $i\theta_2$ being an imaginary hyperbolic angle, may be regarded as a circular angle. In this sense, both of the complex angles β and θ may be considered as being composed of a circular and a hyperbolic component. Moreover, equations (7) and (8), when dealing wholly with the usual real quantities, may be rewritten in the forms:

$$\beta_1 = gd\,\theta_1 \ (\beta_2 = \theta_2 = 0) \quad \text{real cir. radians} \tag{12}$$

$$\theta_1 = gd^{-1}\beta_1 \ (\beta_2 = \theta_2 = 0) \quad \text{real hyp. radians} \tag{13}$$

Methods of Solving Complex Gudermannian Equations.—It can be found, by trial, that any of the gudermannian equations (1) to (8), considered as extended to the complex plane, can be solved for any finite complex value of θ. Thus, let

$$\theta = 0.5 + i\,\underline{0.75} = 0.5 + i\,1.1781 \tag{14}$$

where θ_2 is 1.1781 cir. radians or 0.75 quadrant, or 75 grades, or 67° 30′. Then applying, for instance, equation (1),

$$\sin \beta = \sin (\beta_1 + i\beta_2) = \tanh (0.5 + i\,1.1781)$$

which by Tables,[3] is

$$= 1.40579 + i\,0.84585. \tag{15}$$

This equation may be solved by the use of the same Tables, or by Charts[4] or by known formulas. The solution is:

$$\beta = \beta_1 + i\beta_2 = 0.93737 + i\,1.1547 \quad \text{cir. radians} \tag{16}$$

where $\beta_1 = 0.93737$ circular radians, and $\beta_2 = 1.1547$ hyperbolic radians. This is the complex gudermannian of $\theta = 0.5 + i\,\underline{0.75}$ or $0.5 + i\,1.1781$. The same solution might be found by each and all of equations (1) to (6) taken as complex. The first set of complex gudermannians was obtained in this way, in a problem concerning electrical networks, which suggested the likelihood of such complex angles by physical analogy. There is, however, a shorter method of solution. It may be shown that, given any pair of complex components θ_1 and θ_2,

$$\tan \beta_1 = \frac{\sinh \theta_1}{\cos \theta_2} \tag{17}$$

and

$$\tanh \beta_2 = \frac{\sin \theta_2}{\cosh \theta_1}. \tag{18}$$

We may plot, on a $\beta_1\beta_2$ plane, the points corresponding to successive pairs of $\theta_1\theta_2$. It is evident from (17) and (18), that if we vary θ_2, keeping θ_1 constant, the values of β_1 and β_2 correspond to:

$$\beta_1 = \tan^{-1} (A \sec \theta_2) \tag{19}$$

and

$$\beta_2 = \tanh^{-1} (B \sin \theta_2) \tag{20}$$

where the constants are:

$$A = \sinh \theta_1 \tag{21}$$

$$B = \operatorname{sech} \theta_1. \tag{22}$$

If, on the other hand, we vary θ_1, keeping θ_2 constant,

$$\beta_1 = \tan^{-1}(C \sinh \theta_1) \tag{23}$$

$$\beta_2 = \tanh^{-1}(D \operatorname{sech} \theta_1) \tag{24}$$

where the constants are:

$$C = \sec \theta_2 \tag{25}$$

$$D = \sin \theta_2. \tag{26}$$

Geometrically, equations (19) and (20) lead to a series of closed loops in the $\beta_1\beta_2$ plane, that may be called gudermannian loops of constant real component θ_1; while equations (23) and (24) lead to a series of curves which start from definite points on the β_2 axis, and pass through the center of the θ_1 loops. These curves may be called gudermannian curves of constant imaginary component θ_2.

Principle of Cross-Substitution in Gudermannian Identities.—If we form the equations for antigudermannians or lambertians, we find:

$$\tanh \theta_1 = \frac{\sin \beta_1}{\cosh \beta_2} \tag{27}$$

and

$$\tan \theta_2 = \frac{\sinh \beta_2}{\cos \beta_1} \tag{28}$$

which compare with (17) and (18). In fact, we can form (27) and (28) out of (17) and (18), by mutually exchanging θ_1 and β_2, and likewise θ_2 with β_1. The same graph of gudermannians in the $\beta_1\beta_2$ plane may be converted into a graph of antigudermannians in the $\theta_1\theta_2$ plane, with the aid of this cross substitution. There are a number of such cross-substitution formulas in the theory of gudermannians. For example, taking

$$gd(\theta_1 + i\theta_2) = \beta_1 + i\beta_2 \quad \text{complex circular radians} \tag{29}$$

and cross substituting as above, we have:

$$gd(\beta_2 + i\beta_1) = \theta_2 + i\theta_1 \quad \text{complex circular radians} \tag{30}$$

which is a formula of general application. Thus we have seen that

$$gd(\theta_1 + i\theta_2) = gd(0.5 + i1.1781) = 0.93737 + i1.1547 \tag{31}$$

Cross substituting,

$$gd(1.1547 + i\,0.93737) = 1.1781 + i0.5 \tag{32}$$

Again, if in (29), we assign the value zero to both θ_2 and β_2, thus reducing (29) to (12), the ordinary real gudermannian equation, then (30) becomes:

$$gd(0 + i\beta_1) = (0 + i\theta_1) \tag{33}$$

or simply

$$gd(i\beta_1) = i\theta_1 = i\ gd^{-1}\beta_1 \tag{34}$$

Thus, if we take from existing Tables of real gudermannians the relation

$$gd\ \theta_1 = gd\ 1.615 = \beta_1 = 1.17814; \tag{35}$$

then

$$gd(i1.17814) = i1.615 \tag{36}$$

or the gudermannian of an imaginary hyperbolic angle is its real anti-gudermannian taken as an imaginary. A Table of real gudermannians is therefore also a Table of imaginary gudermannians, when read reversely. In other words, existing Tables of real gudermannians serve also to evaluate imaginary gudermannians, by simple reversion.

Equality of Tangent Products of Components in Complex Angles and Their Gudermannians.—It may be noted that if we multiply (17) by (18), or (27) by (28), we obtain

$$\tan \beta_1 . \tanh \beta_2 = \tanh \theta_1 . \tan \theta_2 = \tan \gamma \tag{37}$$

which means that the tangent products are always equal. The identity also follows from cross substitution. The circular angle $-\gamma$ is that which the tangent to the constant-θ_1 loops makes with the Y-axis, or the tangent to the constant-θ_2 curves makes with the X-axis. In the same graph treated as an antigudermannian graph, these axes exchange.

Practical Applications of Complex Gudermannians.—Complex gudermannians have various applications in physics and electrical engineering. Thus, if an infinite number of very long, equidistant, parallel, coplanar, straight wires are steadily maintained at successively equal and opposite potentials, the two dimensional field of potential-flux distribution in a plane perpendicular to the wires is a gudermannian complex, with equipotentials following loops of constant θ_1 and flux paths following curves of constant θ_2. This distribution has been cleverly worked out and graphed by Dr. Bernard Hague[5] for the corresponding magnetic case in relation to dynamo-electric machines; but in algebraic terms only, and without reference to gudermannians or complex trigonometry. A similar set of curves has also been published, in relation to problems of electrical transmission lines, by R. S. Brown,[6] without explicit gudermannian significance. The forms of complex gudermannian distribution graphs are therefore not new; although their trigonometrical meaning and implication may have escaped attention.

Outline Table of Complex Gudermannians.—The accompanying Table gives values of β_1 and β_2, to four decimal places, for various stepping values of θ_1 and θ_2. Formulas (1) to (6), or (17) and (18), enable, however, the computations to be carried to as many decimal places as existing

TABLE OF COMPLEX GUDERMANNIANS

$gd(\theta_1 + i\theta_2) = \beta_1 + i\beta_2$

for the ranges

θ_1, 0 to 2.5, in steps of 0.5

θ_2, 0 to 2π, in steps of $\pi/8$

θ_2			$\theta_1 = 0$		$\theta_1 = 0.5$		$\theta_1 = 1.0$		$\theta_1 = 1.5$		$\theta_1 = 2.0$		$\theta_1 = 2.5$	
πS	RADIANS	QUADRANTS	β_1	β_2	β_1	β_2	β_1	β_2	β_1	β_2	β_1	β_2	β_1	β_2
0	0	0	0	0	0.4804	0	0.8658	0	1.1317	0	1.3018	0	1.4070	0
$\pi/8$	0.3927	0.25	0	0.4032	0.5135	0.3534	0.9045	0.2533	1.1614	0.1641	1.3214	0.1021	1.4192	0.0625
$2\pi/8$	0.7854	0.5	0	0.8814	0.6351	0.7366	1.0292	0.4951	1.2502	0.3102	1.3782	0.1902	1.4544	0.1158
$3\pi/8$	1.1781	0.75	0	1.6150	0.9374	1.1547	1.2560	0.6912	1.3931	0.4150	1.4657	0.2507	1.5077	0.1518
$\pi/2$	1.5708	1.0	0	∞	1.5708	1.4068	1.5708	0.7719	1.5708	0.4539	1.5708	0.2723	1.5708	0.1645
$5\pi/8$	1.9635	1.25	0	1.6150	2.2042	1.1547	1.8858	0.6912	1.7485	0.4150	1.6759	0.2507	1.6339	0.1518
$3\pi/4$	2.3562	1.5	0	0.8814	2.5065	0.7366	2.1124	0.4951	1.8914	0.3102	1.7634	0.1902	1.6872	0.1158
$7\pi/8$	2.7489	1.75	0	0.4032	2.6281	0.3534	2.2371	0.2533	1.9802	0.1641	1.8202	0.1021	1.7224	0.0625
π	3.1416	2.0	0	0	2.6612	0	2.2758	0	2.0099	0	1.8398	0	1.7346	0
$9\pi/8$	3.5343	2.25	0	−0.4032	2.6281	−0.3534	2.2371	−0.2533	1.9802	−0.1641	1.8202	−0.1021	1.7224	−0.0625
$5\pi/4$	3.9270	2.5	0	−0.8814	2.5065	−0.7366	2.1124	−0.4951	1.8914	−0.3102	1.7634	−0.1902	1.6872	−0.1158
$11\pi/8$	4.3197	2.75	0	−1.6150	2.2042	−1.1547	1.8858	−0.6912	1.7485	−0.4150	1.6759	−0.2507	1.6339	−0.1518
$3\pi/2$	4.7124	3.0	0	$-\infty$	1.5708	−1.4068	1.5708	−0.7719	1.5708	−0.4539	1.5708	−0.2723	1.5708	−0.1645
$13\pi/8$	5.1051	3.25	0	−1.615	0.9374	−1.1547	1.2560	−0.6912	1.3931	−0.4150	1.4657	−0.2507	1.5077	−0.1518
$7\pi/4$	5.4978	3.5	0	−0.8814	0.6351	−0.7366	1.0292	−0.4951	1.2502	−0.3102	1.3782	−0.1902	1.4544	−0.1158
$15\pi/8$	5.8905	3.75	0	−0.4032	0.5135	−0.3534	0.9045	−0.2533	1.1614	−0.1641	1.3214	−0.1021	1.4192	−0.0625
2π	6.2832	4.0	0	0	0.4804	0	0.8658	0	1.1317	0	1.3018	0	1.4070	0

Examples: $gd(0.5 + i\,0.75) = gd(0.5 + i\,1.1781) = 0.9374 + i\,1.1547$ cir. radians

More strictly, $gd[0.5 + i(1.1781 \pm n\pi)] = (0.9374 \pm n\pi) + i\,1.1547$ cir. radians

Again, $gd^{-1}(1.8858 - i\,0.6912) = 1.0 + i\,4.3197 = 1.0 + i\,2.75$ hyp. radians

More strictly, $gd^{-1}\{(1.8858 \pm n\pi) - i\,0.6912\} = 1.0 + i(4.3197 \pm n\pi)$ hyp. radians

Tables of real circular and real hyperbolic functions will justify. It will been seen that for $\theta_1 = 0$, $i\beta_2$ goes to $\pm i\infty$. Beyond $\theta_1 = 2.5$, the values of complex β are confined to a small and nearly circular range, centered at $\beta_1 = \pi/2$, $\beta_2 = 0$. In the Table, θ_2 is given in three different alternative forms, in the first three columns, namely, in terms of π, of radians, and of quadrants, respectively. An ambiguity appears of $\pm n\pi$ radians in the values of β_1 and θ_2, where n is any integer; but ordinarily this does not involve uncertainty in the application of complex gudermannians.

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NEW STUDIES IN POLYMERIZATION
I. POLYMERIZATION OF STYRENE

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In the course of a series of experiments[2] on the rates of auto-oxidation of iso-eugenol, iso-safrol, anethol, styrene, etc., the writer observed an abnormal decrease in the rate of oxygen absorption long before 10% of the substance in question had undergone oxidation. This decrease of the oxidation rate may be attributed to a rapid polymerization of styrene effected and accelerated by some product formed during the initial stages of the oxidation.

In their studies of the polymerization of styrene to metastyrene under the influence of light and of heat by measuring the viscosity of styrene with time, Stobbe and Posnjak[3] have arrived at the conclusion that the increase in the rate of polymerization of preparations that had been allowed to stand at room temperature for 14 days over those of freshly distilled styrene was unquestionably due to the formation in the former of an "Autokatalysator" or a "Polymerizationskern." In the same year Heinmann[4] found that oxygen or ozone effected the polymerization of iso-

prene to rubber, while nine years later Holt, Steimmig and the Badische Company[5] succeeded in accelerating the polymerization of the same substance to rubber by the addition of small quantities of organic peroxides.

Quite recently Moureu and his co-workers[6] demonstrated the existence of some relationship between the auto-oxidation of acrolein and its polymerization to disacryl. They found that the polymerization of acrolein is not effected in the dark provided oxygen is excluded, while it is readily effected by either oxygen or light alone.

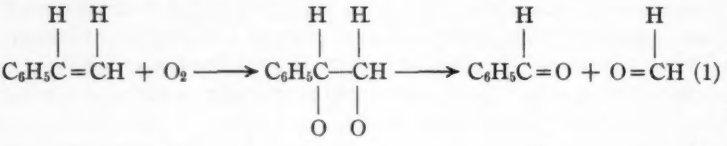
Some preliminary experiments to be presently described show that when small amounts of benzoperacid are added to styrene, the rate of oxygen absorption during the initial stages of its oxidation was considerably increased. A similar phenomenon has been recently observed by Bäckström[7] in the case of benzaldehyde.

The oxygen absorption rates were measured in a special apparatus[2] which permitted a fairly high degree of accuracy. The styrene used was the C. P. grade furnished by the Eastman Kodak Company. Since light, oxygen and long standing[3,4] influence its polymerization, it was further purified just before used by shaking it with a 35% solution of sodium bisulphite, then with a dilute solution of caustic soda and finally with water. The greatest portion of water was then removed by shaking with anhydrous sodium sulphate. It was finally fractionated under diminished pressure in a stream of N_2 which was first bubbled through a solution of pyrogallol in caustic soda, then through conc. sulphuric acid. The fraction boiling at 31° (8 mm.) was collected and kept in a brown bottle under N_2.

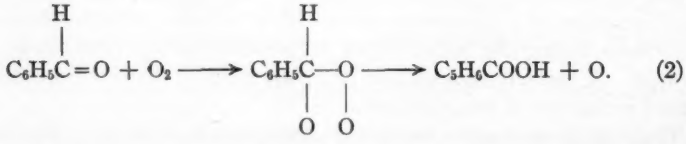
For the preparation of benzoperacid the modified[8] method of Baeyer and Villiger[9] was used. It was found best to add the benzoperacid to a carefully weighed sample of styrene in which it was completely soluble. The entire process of weighing and adding the mixture to the apparatus took, in all measurements, 3 to 3.5 min. No measurements of oxygen absorption were made until the pressure within the apparatus became constant. This usually took 10 to 12 min. The temperature at which the measurements were made was 110 ± 0.1°., and the reaction mixtures were stirred at the rate of 700 ± 15 r.p.m.

The oxidation of styrene alone showed an induction period of 10 min. Curve *A* of figure 1 shows the rate of oxygen absorption of styrene alone, while curve *B* shows the rate of oxygen absorption of styrene + 4% of benzoperacid. The increase in the oxygen absorption rate seems to have caused a corresponding increase in the polymerization rate as shown by the rapid falling of the former during the later stages of the reaction. Experiments are now under way at Massachusetts Institute of Technology using various other auto-oxidants and with more widely varied quantities of benzoperacid.

Selective Inhibition and Induced Oxidation.—The rate of oxidation of styrene alone, as ordinarily measured, is made up of the oxidation rates of two main reactions, .



(1)



(2)

Now, if the polymerization of styrene were due to the absorption of some form of energy, liberated during its oxidation, then, the addition of some substance capable of absorbing part or all of this energy should prevent not only the polymerization of styrene but also inhibit the oxidation of both styrene and benzaldehyde. Bäckström[10] has recently shown that anthracene in a concentration of one mole to 10,000 moles of benzaldehyde decreased the rate of oxidation of the latter at 20° from 0.32 cc. to 0.0025 cc. of oxygen per minute per g. of benzaldehyde (calculated from Bäckström's results). Furthermore, anthracene has been shown to be an excellent absorber of light energy by Weigert[11] and others and was therefore thought to be a suitable substance with which to test the foregoing view. Curve *C* shows the rate of oxygen absorption of styrene in presence of anthracene. The anthracene used was the C. P. quality (a qualitative test showed the absence of anthraquinone) furnished by the Eastman Kodak Company. The concentration used was one mole of anthracene to 10.76 moles of styrene. While the polymerization was completely inhibited, as it will be shown later, the oxidation of styrene proceeded at relatively high rate. For example, after 11 hours the rate of oxidation of styrene + anthracene was 595 cc. per hour per mole of styrene, while that of styrene alone was only 31.8 cc. per hour per mole. An approximate quantitative estimate of the oxidation products of these two reactions is shown in Table 1.

TABLE 1—OXIDATION PRODUCTS OF REACTIONS A AND C; REACTION TIME 11 HOURS

SUBSTANCE	REACTION A [STYRENE]	REACTION C [STYRENE + ANTHRACENE]
Benzaldehyde	0.07 g.	1.8 g.
Benzoic acid	1.1	0.18
Metastyrene	7.3	None
Formic acid	0.16	0.19
Formaldehyde	Traces	ca. 0.2 cc.
Anthraquinone	...	0.85 g.

It may be stated here that anthracene alone, under the conditions of the experiment, was *not* oxidized. The results seem to indicate that anthracene inhibits strongly the oxidation of benzaldehyde but only very slightly

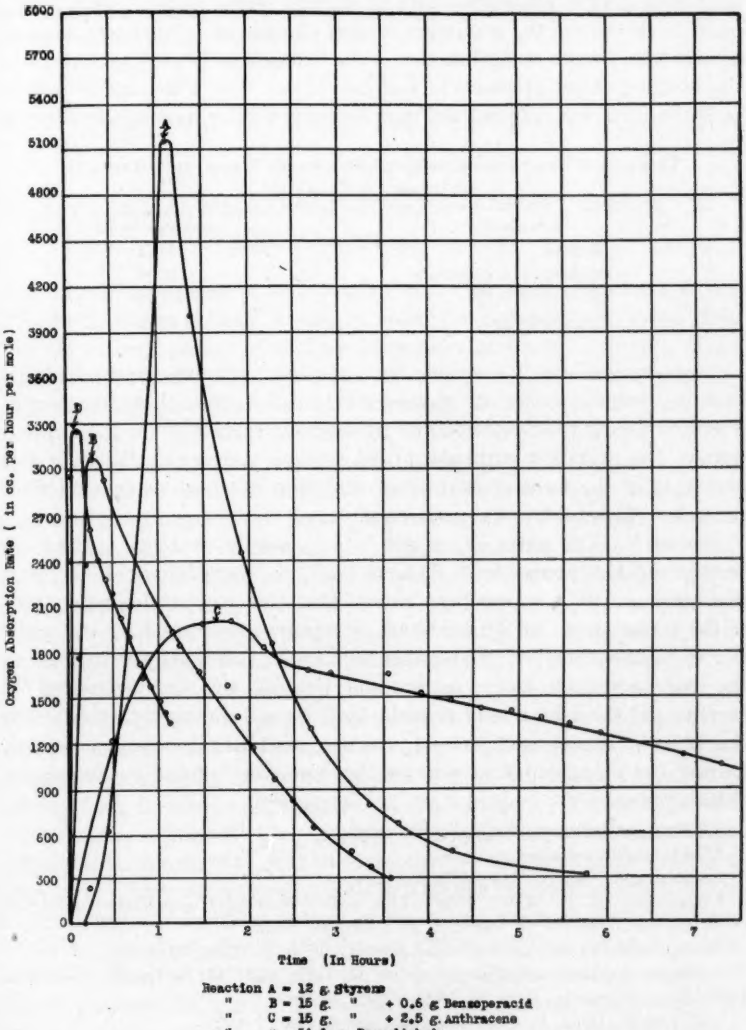


FIGURE 1

that of styrene.[12] The oxidation of styrene in the presence of anthracene therefore seems to show the phenomenon of selective inhibition.

A comparison of the maximum oxygen absorption rate of styrene and styrene + anthracene with that of benzaldehyde shown by curve *D* seems to be of considerable interest. Under similar experimental conditions, the maximum oxygen absorption rate of styrene seems to be, within 3.4%, equal to the sum of the maximum oxygen absorption rates of pure benzaldehyde and styrene + anthracene. The benzaldehyde used was fractionally distilled at low pressures in a stream of dry N_2. The fraction boiling at 89° (4 mm.) was collected and used for oxygen absorption measurements.

TABLE 2—A COMPARISON OF MAXIMUM OXYGEN ABSORPTION RATES OF REACTIONS A, C AND D

SUBSTANCE	MAXIMUM O_2 ABSORPTION RATE IN CC./HR./MOLE
Styrene	5144
Styrene + Anthracene	2000
[S − (S + A)]	3144
Benzaldehyde	3255

One may tentatively conclude from the foregoing experimental results that the polymerization of styrene seems to be effected by the energy liberated during the formation and subsequent reaction of the initial products of the oxidation with unoxidized styrene molecules. Whether this energy is in the form of heat or of radiation of short wave-lengths, it remains to be established experimentally.

Summary.—The rates of oxygen absorption of styrene, styrene + benzoperacid, styrene + anthracene and of benzaldehyde have been measured at 110°. It has been shown that the oxygen absorption rate of the initial stages of the oxidation of styrene is increased by the addition of benzoperacid and this increase seems to be followed by an increase in the polymerization rate. Anthracene inhibits the polymerization of styrene and the oxidation of benzaldehyde formed during the oxidation of the latter. The phenomenon of selective inhibition has been observed. During the oxidation of styrene, anthracene was inducedly oxidized to anthraquinone.

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[10] Bäckström, *J. Am. Chem. Soc.*, **49**, 1460, 1927.

[11] Weigert, *Ber.*, **42**, 850, 1783, 1909.

[12] Anethol with each of the following substances showed analogous results: (1) anthracene, (2) naphthalene, (3) phenanthrene, (4) cymene and (5) succinic acid. In the case of anthracene only traces of anisic acid were obtained, while as high as 20–22% anisaldehyde and 65–70% anthraquinone were isolated. With anethol alone, only traces of anisaldehyde and relatively large quantities of anisic acid were obtained. Details of these experiments will be reported elsewhere.

THE QUENCHING OF CADMIUM RESONANCE RADIATION

BY JOHN R. BATES

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Communicated August 18, 1928

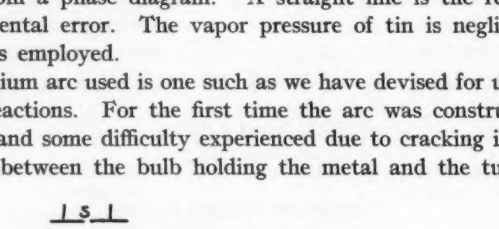
In a previous paper it was pointed[1] out that cadmium atoms in the 2^3P_1 state do not activate hydrogen molecules sufficiently to cause them to react with ethylene, nor do they decompose ammonia. Mercury atoms in this state of activation, however, are able to do both these things.[2,3,4] This was attributed[1] to the fact that the energy of the 2^3P_1 state of cadmium (87,000 cals.) is less than the heat of dissociation of hydrogen (104,000 cals.), while that of mercury is in excess of this value (112,000 cals.). Very few hydrogen molecules would have sufficient thermal energy to make up this deficit and cause dissociation. By raising the temperature, however, the number should be increased and this increase should obey the equations for the temperature coefficient of photochemical reactions as worked out by Tolman.[5]

This work represents an attempt to study this by measuring the quenching of the resonance radiation of cadmium by admixted hydrogen.

The method used is essentially that of Stewart,[6] with necessary changes due to the difference in the physical properties of mercury and cadmium. This can best be seen by reference to figure 1. Two quartz tubes R and Q are mounted side by side in a furnace A with two openings, protected by heating coils to avoid condensation on the windows. These tubes were coated on the inside with lampblack in all places except the two windows and the sides which were next to each other to cut down stray radiation. They were connected by graded seals to a source of cadmium vapor in the adjacent furnace B. The control of the vapor pressure was a problem which at the offset offered considerable difficulties, but which has been solved by means of the "cut-offs" shown in the figure, in which are placed a 50% cadmium-tin alloy. The alloy is a liquid at the temperature at which the cadmium vapor pressure is of the order of magnitude desired, and so may be used to shut the cells off from the rest of the apparatus by lowering the plunger into the pool of metal and forcing it up around the entering tube.

By cutting the cells off in this manner, uncertainties due to the diffusion of the cadmium vapor are eliminated. The vapor pressure above the alloy can be shown to be that of a perfect solution by plotting the reciprocal of the temperature against the logarithim of the concentration, as determined from a phase diagram.[7] A straight line is the result, within the experimental error. The vapor pressure of tin is negligible at the temperatures employed.

The cadmium arc used is one such as we have devised for use in photosensitized reactions. For the first time the arc was constructed in the laboratory, and some difficulty experienced due to cracking in the longer stretch left between the bulb holding the metal and the tungsten seal.



Shortening of this is not practical, because of the graded seal, and so the tungsten wire was extended up to the bulb and surrounded with ground quartz, which is degassed before the metal, melted in vacuo, is admitted. The surface tension of the cadmium prevents it from going into the graded seal and all cracking eliminated.

The light from the arc is focused upon tube R by means of two condensing quartz lenses. R acts as a source of monochromatic resonance radiation, part of which is absorbed by cadmium vapor in Q and either re-emitted, or quenched by the hydrogen. This is determined by the light entering the slit of the spectrograph S. The use of the resonance lamp R is necessary, for the addition of foreign gases broadens the absorption line of the cadmium and makes determinations of quenching impossible.

The intensity of the fluorescent light is measured by assuming the reciprocal law ($IT = D$) for the blackening of photographic plates to hold and calibrating each plate by exposures of the same intensity, I, for different lengths of time, T. If, then, the product of the two is constant, the same blackening would be produced by exposing for the same time and corresponding changes in intensity. While this, at its best, is an inaccurate method, the weak intensity of the fluorescent light and the presence of high temperatures in the furnace made more accurate methods of little use, as will be pointed out later.

The exposures were for a period of 90 minutes and the calibration exposures for 60, 45, 30, 15 minutes. The tubes R and Q were at 250°C. and at 275°, at which temperature the vapor pressure of cadmium is 0.004 mm. and 0.015 mm.

The results show that hydrogen quenches the resonance radiation of cadmium as effectively as it does that of mercury. This fact has much significance from several standpoints. It is quite certain that hydrogen atoms are not produced by these collisions. The probability of this occurring is about 10^{-4} that of the mercury and the quenching would be of the same order of magnitude if this were the process involved in the quenching.

The transfer of energy of excitation of 2^3P_1 state of cadmium which amounts to 3.78 volts, to the hydrogen molecule can only result in an increase in vibrational energy of the latter. There are no electronic levels in the molecule as low as this and and dissipation of this much energy as translation or rotation would not be probable. There is no reason why such a transfer should not result in increased vibrational energy, since mercury atoms can give up their energy of excitation to produce such vibration in the hydrogen molecule as to cause dissociation. Furthermore, there is a vibration level in the hydrogen molecule at 3.84 volts, which is quite close to the 3.78 value of cadmium. This is also in good accord with the recent theory of Kaplan[8] of the spectra obtained by the recombination of hydrogen atoms in the presence of metallic vapors.

The unexpectedly large quenching precluded the attempt to study the temperature coefficient of the reaction between cadmium atoms in the 2^3P_1 state and hydrogen molecules to give hydrogen atoms. In order to see if there was any temperature coefficient of the quenching due to change in probabilities of different vibrational states of hydrogen being involved, a quartz photoelectric cell with a slit and movable table was substituted for the photographic plate, but the intensity of the 3262 line was too small to be recorded even on an electrometer. With a Corning filter instead of the spectrograph, the resonance light was too small a fraction of the total radiation entering the cell to do anything but show that quenching occurred. (I am indebted to Mr. W. B. Nottingham of the Bartol Research

Foundation for advice in the construction of the photoelectric cell.) The design of the attachment of the cell to the spectrograph to make a photoelectric spectro-photometer will be recorded in another place.

The fact that hydrogen molecules, even with 3.78 volts will not react with ethylene is of much interest in reference to the activation theory of chemical reactions. The reaction

$$H_2 + C_2H_4 \longrightarrow C_2H_6$$

is itself exothermic and yet will not occur even with activation of the hydrogen amounting to 87,000 calories. It brings up the consideration, which has often been stated but not with such direct evidence, that the thermal activation of the reactants is in many cases of minor importance in causing reactions to take place; that it is the activation of some catalytic substance which may be present either as an impurity or "wall" which is the major factor in bringing them about.

This work was done while the writer was a National Research Fellow at The Johns Hopkins University, and he takes this opportunity of thanking those who made his year there one of pleasure and profit.

[1] Bates and Taylor, *J. A. C. S.*, **50**, 771 (1928).

[2] Bates and Taylor, *Proc. Nat. Acad. Sci.*, **12**, 714 (1926); *J. A. C. S.*, **49**, 2438 (1927).

[3] Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

[4] Olsen and Meyers, *J. A. C. S.*, **48**, 389 (1926).

[5] Tolman, *J. A. C. S.*, **42**, 2506 (1920); **45**, 2285 (1923).

[6] Stewart, *Z. Physik*, **32**, 262 (1925).

[7] See Johnston and Andrews, *J. Inst. Metals*, **32**, 285 (1924).

[8] Kaplan, *Phys. Rev.*, **31**, 997 (1928).

THE INFLUENCE OF FOOD UPON LONGEVITY[1]

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Communicated September 19, 1928

Accepting the view that longevity is largely and perhaps chiefly determined by inheritance, it still remains possible that other factors may have more influence than has hitherto been clearly demonstrated. Thus if the mode of investigation is to inquire into the histories of people who have attained to noteworthy longevity, the ages reached by their parents and grandparents will usually stand out as clear-cut quantitative data while a correspondingly definite record of the kinds and amounts of foods consumed during a lifetime would be quite unobtainable. With man, one can neither control the food intake throughout a lifetime nor ensure

life-long uniformity of other factors for individuals whose food habits are different. These conditions can, however, be realized experimentally with suitable animals such as the familiar albino rat of the laboratory,[2] amenable to complete control, and having a life cycle not too long to permit of uninterrupted observation. It is also of interest that in general food habits and mode of metabolism of foodstuffs, as indicated by the end products appearing in the urine,[3] the rat is so much like the human as to justify considerable confidence that nutritional principles demonstrated in the one species will probably apply also to the other.

We have recently completed a somewhat extended experiment in which the influence of a single change in the food supply upon the longevity of rats of identical heredity, maintained under conditions uniform in all other respects, appears to have been fully demonstrated.

One of the groups of experimental animals received Diet *A*, a mixture of one-sixth dried whole milk and five-sixths ground whole wheat with table salt in the proportion of two per cent of the weight of the wheat, and distilled water *ad libitum*. The parallel group received Diet *B*, which differed from Diet *A* only in that the proportion of dried milk was increased to one-third, the wheat becoming two-thirds. We have previously outlined elsewhere[4] our mode of conducting such experiments and the evidence, from rates of growth and reproduction records, that Diet *A* is adequate but Diet *B* is better.

About two hundred animals, the exact numbers being 220 upon Diet *A* and 179 upon Diet *B*, were kept continuously upon each of the two diets until natural death.

With both males and females the average duration of life was almost exactly ten per cent longer upon Diet *B* than upon Diet *A*. The data are summarized in table 1.

TABLE 1

COMPARISON OF LONGEVITY OF RATS ON DIETS A AND B

	DIET A		DIET B		DIFFERENCE
	NUMBER OF CASES	LENGTH OF LIFE IN DAYS	NUMBER OF CASES	LENGTH OF LIFE IN DAYS	OF LENGTH OF LIFE IN DAYS
Males	92	576 ± 10.0	80	635 ± 12.9	59 ± 16.0
Females	128	604 ± 11.4	99	664 ± 11.5	60 ± 16.2

The average lengths of life as given in table 1 are followed by estimates of their probable errors computed in the usual manner. It is realized that the validity of such computation of probable error might be questioned on the ground that it assumes a symmetrical frequency distribution which has not been actually demonstrated for data of this particular kind. It may be said, however, that the cases here summarized, while not sufficiently numerous to afford smooth diagrams, indicate at least an approximation to the symmetrical frequency distribution; and they belong to the general category of natural phenomena to which, according to Reitz and Mitchell,[5]

the usual calculations of probability may normally be expected to be applicable. Both for males and for females, the difference between the mean lengths of life upon the two diets is 3.7 times its probable error, as computed by the usual method. Assuming that this method is even approximately correct for the data here considered, this would mean that the chances that the differences found are truly significant and not accidental are about of the order of one hundred to one.

The reality of the observed differences in longevity is also confirmed in other ways.

If the median length of life be compared, instead of the mean, both males and females again show the distinct difference in favor of Diet *B*.

Furthermore, if we compare the percentages of individuals attaining to definite degrees or standards of longevity, we find that such cases of longevity are distinctly more frequent upon Diet *B* than upon Diet *A*, as may be seen from the data summarized in table 2.

TABLE 2

INFLUENCE OF FOOD UPON ATTAINMENT OF DEFINITE DEGREES OF LONGEVITY

	PERCENTAGE OF RATS LIVING OVER 800 DAYS	PERCENTAGE OF RATS LIVING OVER 900 DAYS
Males		
Diet A	4.3	0.0
Diet B	13.8	2.5
Females		
Diet A	17.2	3.9
Diet B	20.2	9.1

Here it will be seen that when the results are so arranged as to test the influence of food upon the attainment of definite degrees of longevity there is, in each of the four comparisons, again a distinct difference in favor of Diet *B*.

Infant mortality is not included in the data discussed in this paper; if it were, the differences in favor of Diet *B* would be still further accentuated.

It is especially worthy of emphasis that the influence of food upon longevity, as here recorded, was manifested well within the bounds of normal and adequate nutrition. Reference has been made above to an earlier paper[4] giving numerous data which establish the adequacy of Diet *A*, and it may also be said in this connection that we now have rat families in our colony which are still thriving upon this diet in the twenty-first generation.

Diet *A* is therefore adequate, but not optimal. Diet *B* is better than Diet *A*, but is doubtless still capable of further improvement. Hence it is probable that further studies will reveal possibilities of a more extended influence of food upon longevity than that here recorded.

The precise determination and relative evaluation of the individual chemical factors involved will doubtless require prolonged investigation.

[1] This paper is published as Contribution No. 589 from the Department of Chemistry, Columbia University.

[2] For discussion of the rat as a laboratory animal for nutrition investigations, see Osborne, T. B., and Mendel, L. B., Publication No. 156, Carnegie Institution of Washington (1911).

[3] Folin, O., and Morris, J. L., *J. Biol. Chem.*, **14**, 509–515, 1913.

[4] Sherman, H. C., and Campbell, H. L., *J. Biol. Chem.*, **60**, 5–15, 1924.

[5] Reitz, H. L., and Mitchell, H. H., *J. Biol. Chem.*, **8**, 297–326, 1910–11.

THE INTERFEROMETER U-GAUGE WITH CLOSED AUXILIARY RESERVOIRS

BY CARL BARUS

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Communicated October 9, 1928

1. *Both Reservoirs of the U-Gauge Closed.*—In the doubly closed gauge either shank becomes a region for the measurement of small pressures, provided the temperature differences can be adequately stated. To facilitate this, the air space v (figure 1, insert g) and the air space v' are severally connected with identical Dewar flasks of relatively large volumes, D and D', each provided with a sensitive thermometer T, T', reading at least to 0.01°C.

Since the micrometer of the interferometer is adjusted to indicate pressure on the v' side, if its readings increase, the equation heretofore* used now becomes

$$dh + h(dh/2l + d\tau/\tau) = \Delta h + h(-dh/2l + d\tau'/\tau),$$

dh being the total change of head when the level falls in v', τ denoting absolute temperature (rising in both cases), h the mean barometer height and l the modified depth of the volumes v, v', computed to include the volumes of D and D' for the same diameter of gauge level at m and m'. Hence

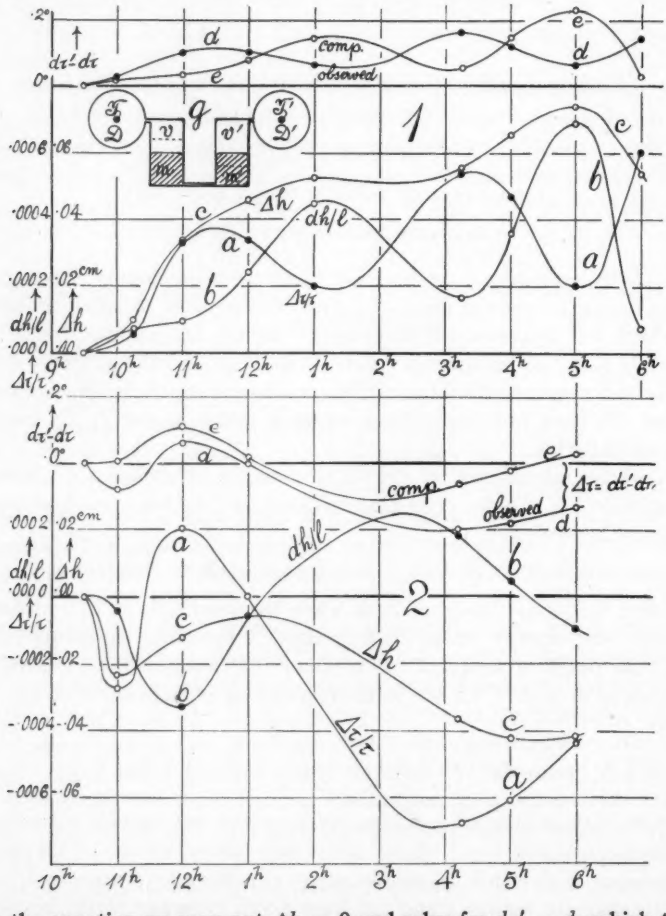
$$\Delta h = dh + h\left(\frac{d\tau - d\tau'}{\tau} + dh/l\right) = 0,$$

since dh is the whole head of mercury as stated and there is no pressure-producing reaction in v'. Thus Δh is here an indication of the degree of accuracy with which the temperatures τ, τ' have been measured.

2. *Data.*—In figures 1 and 2 I have given examples of the results of four runs taken on successive days between 9 A.M. and 6 P.M., as shown by the abscissas. The curves a summarize the temperature changes in the lapse of time, where $\tau' - \tau$ was always positive and $d\tau' - d\tau$ also as a rule and hence the quantity $(d\tau' - d\tau)/\tau = \Delta\tau/\tau$ has been plotted

in preference to the term in the equation. Difference in the fixed points of the thermometers are of no concern.

The curves b show the successive variations of mercury head dh, where dh/l reciprocates with $\Delta\tau/\tau$ if Δh is zero. The curves a and b give evidence of a partial tendency to do this, but in the curve c, the value of the spurious Δh is none the less striking in all cases.



In the equation we may put $\Delta h = 0$ and solve for $d\tau' - d\tau$ which then becomes $\tau dh(1/h + 1/l) = \tau dh(0.0132 + 0.125) = 41.2\ dh$, if as heretofore $\tau = 296°$ $h = 76$ cm., $l = 8$ cm. The temperature differences $d\tau' - d\tau$ computed in this way are given in curves e, and the corresponding observed temperature differences in curves d.

In figure 1, though the reciprocation of $d\tau$ and dh curves is marked, the Δh curve rises in the course of the day to nearly 0.07 cm. of mercury. The apparatus was so frequently overhauled, that any leak in the apparatus (though there is no way of testing for it) is highly improbable. The explanation is suggested by the curves d and e, of which the latter (given by dh) is an instantaneous result, while the former given by the mercury thermometers T, T', lags. Thus if the d curves were shoved to the right about 1.5 hours, there would be better coincidence and the serious discrepancy of 0.1°C. would be largely eliminated. Toward the evening, however, the temperature error usually increases.

The significant values of Δh then show that an environment whose temperature varies even as little as one-tenth degree per hour, will not enable us to measure small pressure increments, if mercury thermometers, however sensitive, are used. It should be nearer 0.1° per day. True, the use of thermocouples in D and D' (or of a single differential couple) suggests itself; but this would unduly complicate the procedure.

Figure 2 exhibits variations of a new kind, of which thermometer lag as shown by the curves d and e is no longer an adequate explanation, for troughs and crests here correspond pretty well. The $(d\tau' - d\tau')/\tau$ curve is largely negative; in other cases it was quite so. Moreover, in figure 2, Δh is negative throughout, the only case in which this was found. Nevertheless the reciprocation of a and b curves is in general good, apparently. In figure 2, dh/l passes through zero (not counting the beginning) twice, but only once (at 1^h) does Δh tend to do so. Any adequate explanation would thus be very complicated. In general, however, the remarks made for figure 1 apply to all the series.

* These PROCEEDINGS, **14**, 1928, p. 641.

CHARACTERISTIC DIFFERENTIATION IN THE SPECTRA OF SATURATED HYDROCARBONS

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Communicated September 29, 1928

The vibration spectrum occurring in the near infra-red offers the most promising approach to the problem of structure of those polyatomic molecules for which great moment of inertia precludes resolution of the rotation spectrum. The failure of earlier investigations to lead to conclusions of greater value has been largely due to the inadequacy of the observational data. Higher resolving power not only may strengthen conclusions based upon numerical coincidence, but offers in the increased

detail information of real value. In a preliminary investigation of the saturated hydrocarbons definite differentiation was observed between successive members of the paraffine series. In the more detailed study, results of which are presented here, spectral characteristics have been observed which may have an important bearing upon the theories of organic chemistry.

Although the vibration spectrum does not offer immediate knowledge of the structural dimensions, such as has been furnished by the rotation spectrum through moments of inertia, it does furnish information as to the binding forces. To a first approximation, the binding force may be treated as proportional to the square of the frequency, where the effective mass may be considered identical, differing little from that of the hydrogen atom. In dealing with binding forces between the hydrogen and carbon atoms of the hydrocarbons, one may reasonably assume the heat of dissociation to be functionally dependent upon the binding forces. In fact, in a homologous series such as this, because of the necessary similarity in the types of binding, the heats may closely approach linearity in the relation to binding force. If one is then able to identify strictly analogous vibration frequencies of different hydrogens, the possibility presents itself of making this a basis for the study of relative heats of dissociation of the hydrogens in different positions.

The natural attempt to identify certain spectral characteristics with constituents or radicals is fraught with considerable danger. Rigidly, the whole molecule must be regarded as a single system. Any modification of the molecule will modify the normal coördinates. Yet if loosely bound units go to form the molecule, certain modes of vibration must closely approach those which would be exhibited by an isolated unit. Thus the hydrogens associated with a single carbon may form a unit sufficiently loosely coupled to other units to furnish identifying characteristics.

Further, certain of the vibrations of the hydrogen atoms may be identified by this similarity of frequency with that of an hypothetical H-C molecule, if it were to form an isolated system without change in binding force. The vibration frequency attributed to actual CH has a frequency of from 2797 to 2815 cm.$^{-1}$. Of the maxima observed by Coblentz as characteristic of CH_2 and of CH_3 groups,

$$3.43\mu \qquad 6.86\mu \qquad 13.6\text{–}14\mu,$$

this argument tends to identify the 3.43 band (frequency of 2921 cm.$^{-1}$) as of the right order of magnitude for a mode of vibration most similar to that of the hypothetical H-C diatomic molecule. Other considerations support this view. Despite the frequency relation which suggests that 3.43μ be the first overtone of 6.86μ, it behaves in many respects as a fundamental. Regarding 6.86μ as the fundamental, the bands appear-

ing at frequencies of about the correct values exhibit intensities of an alternating character which throws doubt upon that interpretation. Furthermore, the 6.86μ band and the alternate bands which would be related to it, but not to 3.43μ, as overtones, are more affected as to frequency by modifications of the molecule than the others. The most reasonable conclusion would seem to be that a new fundamental occurs in the paraffine series at 3.43μ practically coincident with the overtones of the fundamental at longer wave-length (6.86μ).

Figure 1 shows the absorption spectrum of (*a*) *n*-octane, (*b*) *n*-heptane, (*c*) *n*-hexane, (*d*) iso-pentane as it appears upon the emission at a tungsten

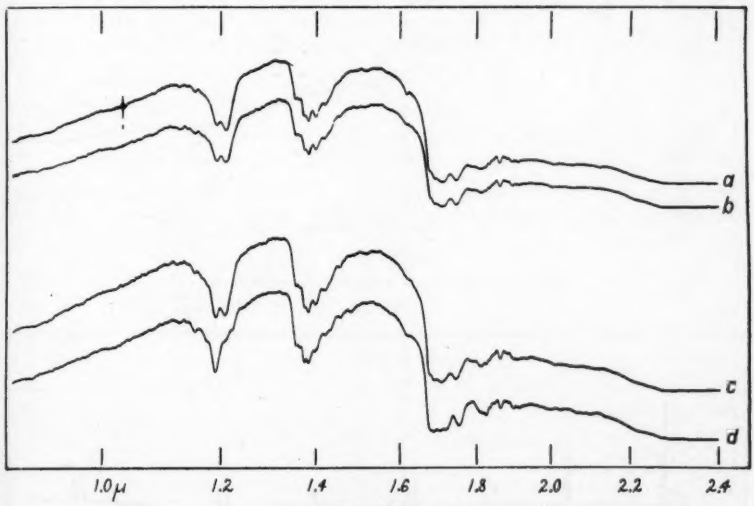

FIGURE 1

Absorption spectrum of the normal hydrocarbons, (*a*) *n*-octane, (*b*) *n*-heptane, (*c*) *n*-hexane, (*d*) iso-pentane. Cell 4 mm. thickness.

filament at 3000°C., shown directly in figure 2. Here it will be observed that marked differentiation is exhibited in the 1.2μ band. In the classical sense this would be the second overtone or third harmonic of the 3.43μ band. A study of it has the advantage over the study of 3.43 or 1.72μ, that the superposed overtones of the 6.86μ bands decreasing rapidly in intensity should not be expected to exert much influence upon it.

This differentiation suggests that the long wave component be identified with the hydrogens of the secondary carbon or the intermediate units of the chain. In the progression *n*-hexane (*c*), *n*-heptane (*b*) and *n*-octane (*a*), its relative intensity markedly increased, as would be expected with the increase in number of intermediate units. Then identifying the short

wave component with the end or methyl group, our hypothesis is strengthened by its predominance in the case of (*d*) iso-pentane (2) methylbutane, where there are three methyl groups, only one secondary and one tertiary group as against two methyl and three secondary groups of *n*-pentane which would occupy position (*d*) in normal progression. This must not be interpreted as arguing that necessarily the groups CH_2 or CH_3 actually each present but a single component in this region, but simply that these frequencies identified seemed to dominate and are assumed to be

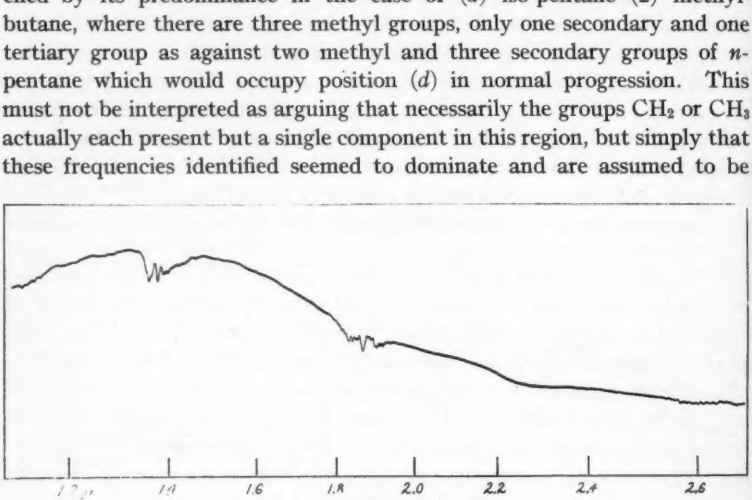

FIGURE 2
Spectrum of source without absorption cell.

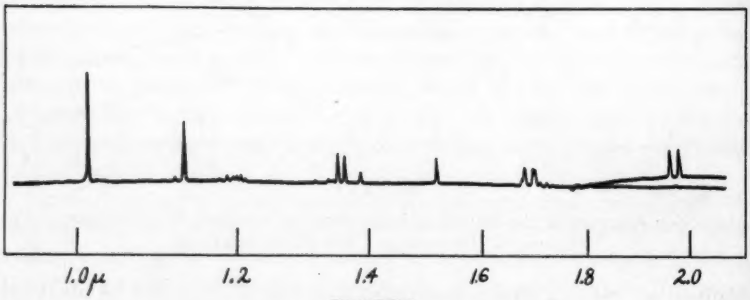

FIGURE 3
Emission spectrum of mercury. Slit width 30 Å.

homologous. If so, one is able to determine the relative values of the force constants on the basis of the simplest possible assumptions.

The preliminary work (Fig. 1) was carried out at a resolving power of about 30 Å to the slit width, both slits being alike. The materials used were of Kalbaum preparation. The results are so suggestive, offering as they do, a possible means of gaining information as to binding force and heat of dissociation of the different types of groups which typify the hydrocarbons, that a more extended investigation seemed justified.

Through coöperation with the Fixed Nitrogen Research Laboratory, especially purified materials were prepared by Dr. A. Lachman. The resolving power was increased to about 12 Å to the slit width. Through the stability of the automatic recording spectrograph, the intensities can be determined with great accuracy. The slight variations due to the variation in current in the continuous source present in the preliminary investigation (Fig. 1) have been eliminated by the use of a large storage battery devoted solely to this work. Thus figure 2 readily shows the atmospheric water vapor absorption at 1.1μ, 1.4μ, 1.9μ and 2.6μ. These serve as a ready basis for wave-length identification as they can be recognized in all the plates. The dispersion curve has been obtained

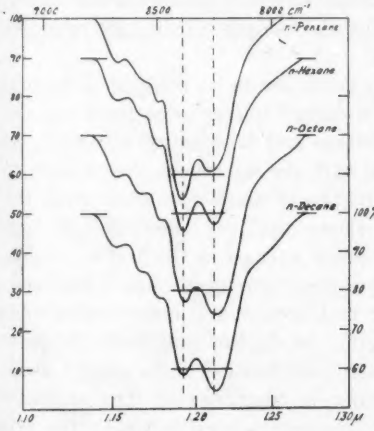

FIGURE 4
Transmission of the normal hydrocarbons. Slit width 12 Å. Cell 4 mm.

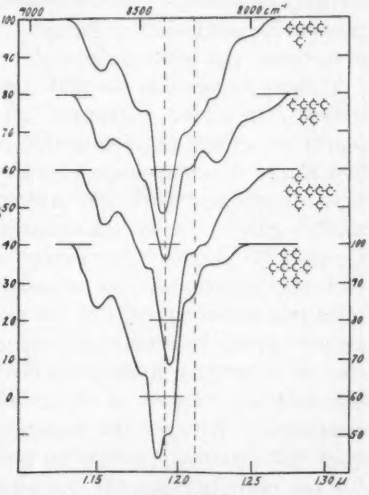

FIGURE 5
Transmission of the isomeric hydrocarbons. Slit width 12 Å. Cell 4 mm.

from the mercury emission spectrum. These figures 1, 2, 3 and 6 mentioned later, are all part of the preliminary investigation carried out at the resolving power 30 Å slit width. The results of more extended investigation at higher resolving power are presented in figures 4 and 5. The transmission of a four-millimeter cell has been plotted as a function of wave-length (indicated at the lower edge of the graph) or frequency in cm.$^{-1}$ (indicated at the upper edge of the graph). This graph has been made by measurement of the original direct records.

Figure 4 shows the normal compounds, while figure 5 deals with certain isomers. The differentiation observed in the preliminary work is evident. Furthermore, although the short wave component shows almost no varia-

tion in frequency (perhaps a slight shift to longer wave-lengths), the long wave component shows a marked shift of center of gravity to longer wave-lengths with the increase of length of chain. This possibly shows that the secondary groups contiguous to the end or methyl group exhibit a slightly greater frequency or binding force than those near the middle of the chain.

In addition to the dominating doublet which has been discussed, three well-defined frequencies appear at shorter wave-lengths. The middle of these enhances in strength with the increase of strength of the long wave component of the "doublet," which suggests that it be identified with the secondary group. Thus the methyl group CH_3 probably presents at least a triplet in this region and the secondary CH_2 at least a doublet. Considering the complexity of the spectra of the halogen substitution products of methane, this is not surprising.*

Turning to figure 5, the first (top) curve shows iso-pentane (2 methyl butane), the second, iso-hexane (2,3-di-methyl butane), the third and the fourth iso-octanes (2,2,4-trimethyl pentane and hexamethyl ethane). At first glance the components identified with the secondary groups seem to have disappeared with the predominance of those identified with the methyl group. Closer examination shows that the absorption in that region of the dominant component is much stronger in the first and third, each of which contain one secondary group. In the second, which contains two tertiary groups of but one hydrogen, a still longer wave component appears of considerable strength. In the first and third, the presence of the tertiary group is less marked, both because of the smaller number, and also because of the proximity in frequency of the secondary component. Between the dominant frequencies identified with the primary and secondary groups we observe a difference of 133.33 cm.$^{-1}$, or 1.6 per cent, between the secondary and tertiary, a difference in frequency of 100 cm.$^{-1}$, or 1.2 per cent. This would mean on the above hypothesis 3.2 per cent and 2.4 per cent difference in binding force, respectively, and a relative difference in heats of dissociation of hydrogen in these different positions of about that proportion, decreasing of course in the order mentioned.

In the preliminary investigation, the benzene spectrum (Fig. 6) was found to present a slight doubling of the corresponding band. In this case we have no basis for an identification of the components with the different hydrogenic oscillators. If, however, that assumption be made, we can at least set an outside limit on the difference which may exist between the binding of the hydrogen atoms in different positions. The frequency separation being only 50 cm.$^{-1}$, corresponds to a difference of binding force on such a basis, slightly less than 1.2 per cent. Since there is reasonable doubt as to the identification of the components of the

"doublet" with the different hydrogenic oscillators, there is no reason to conclude that there may not be complete identity. The practical or complete equality of binding force for hydrogens of different positions is consistent with the prevailing ideas of organic chemistry. It is found that the mean position of the band in benzene is 8750 cm.$^{-1}$, as compared with 8322 cm.$^{-1}$ in the paraffines, i.e., a five per cent greater frequency or ten per cent greater binding force, if one is justified in pushing this argument so far, where the nature of the binding is no longer strictly similar. Benzene shows a very interesting fine structure of low frequency superposed vibration. This has also been studied under high dispersion and the results of the analysis will be published in the near future.

In a paper referred to the author in manuscript, Ellis has observed the

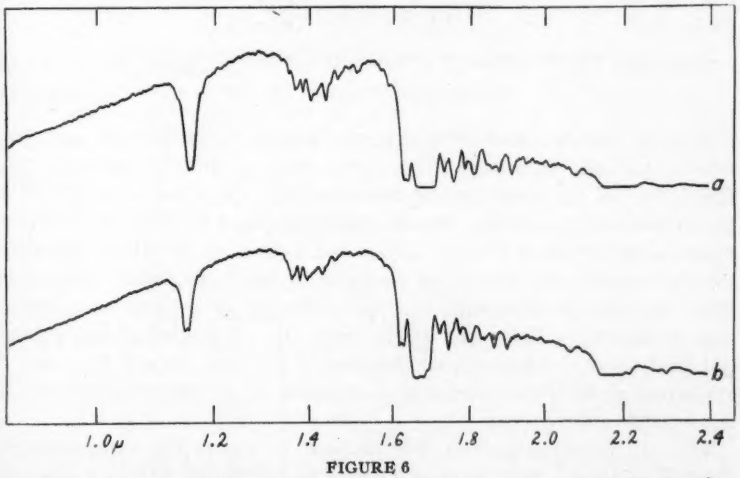

FIGURE 6

Absorption spectrum of benzene, (*a*) 1 cm. cell. (*b*) 4 mm. cell. Slit width 12 Å.

doubling of hexane in the visible higher members of this series. By an extension of the series he has arrived at a value of the heat of dissociation of hydrogen from hexane and several other organic compounds. Because of the lack of sufficient infra-red data, he could only use the average values of the frequency. It is hoped in the near future by coöperative effort to determine the heats of dissociation, using the separate components as found in his work in the visible and our work in the infra-red.

Conclusions.—Differentiation has been observed in the spectrum of the saturated hydrocarbon which forms a basis for the determination of the relative binding forces exerted upon the hydrogens when attached to the primary, secondary and tertiary carbons. A very small upper limit has been placed upon the possible difference in binding of the different hydro-

gens in benzene. It is pointed out that the binding force in benzene is considerably greater than in the saturated hydrocarbons.

This work has been made possible through the coöperation of the Fixed Nitrogen Research Laboratory with the University of California. It gives me pleasure to express my appreciation to Dr. A. Lachman for his help and interest.

* The Infra-Red Absorption Spectra of the Halogen Derivatives of Methane, *Ast. J.*, LXVII, **3**, 1928.

ARE CHARACTERISTIC X-RAYS POLARIZED?

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Communicated October 13, 1928

In 1905 Barkla[1] discovered that the general radiation from an x-ray tube is partially polarized. The recent work of Bishop[2] indicates that this is true of the characteristic radiation from the x-ray tube as well as the continuous spectrum. Bishop analyzed the x-rays by scattering at ninety degrees from a block of carbon and measuring the relative intensity for the vertical and horizontal positions of the x-ray tube. He used a filter method for separating out the radiation of desired wave-length, thus preserving a large part of the intensity. Havighurst[3] has pointed out that, if the characteristic radiation is partially polarized, values of the structure factor as ordinarily determined by crystal reflection will be appreciably altered.

Due to its importance it was decided to repeat the experiment by another method. This method is based on integrated intensity measurements. The usual factor $\frac{1}{2}(1 + \cos^2 2\theta)$, contained in equations for scattering and integrated intensity, applies only when the primary beam is unpolarized. If the primary beam is partially polarized, the factor is a function of the position of the x-ray tube except when the cathode stream makes an angle of 45° with the plane of incidence of the reflecting crystal.

Kirkpatrick[4] has shown that if the integrated reflection from a crystal is compared for the vertical and horizontal positions of the x-ray tube, the polarization of the primary beam is given by

$$P = \frac{1 - K\cos^2 2\theta}{K - \cos^2 2\theta} \qquad (1)$$

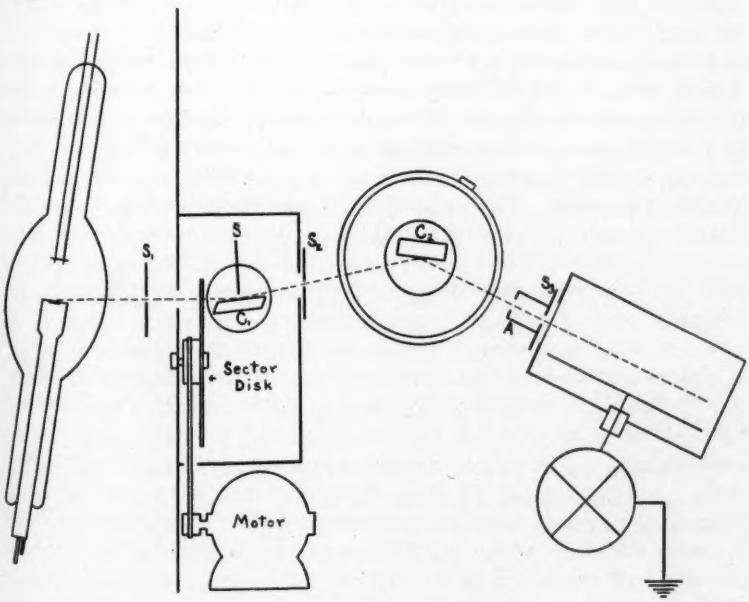
In this expression the polarization $P = E_\perp^2/E_\parallel^2$, where $E_\perp$ and $E_\parallel$ are the electric vectors perpendicular and parallel to the electron stream,

θ is the glancing angle for the crystal, and $K = \frac{(E\omega/I)_V}{(E\omega/I)_H}$, in which $(E\omega/I)_V$ and $(E\omega/I)_H$ are the integrated intensities for the vertical and horizontal position of the x-ray tube. In the term $(E\omega/I)$, E is the energy in the reflected beam, ω is the angular velocity with which the crystal is turned and I is the intensity of the primary beam. Hence by observing the integrated intensity in the two positions of the x-ray tube the degree of polarization can be calculated.

In the experimental determination of $E\omega/I$ it is customary to render the primary beam homogeneous by reflection from a crystal. In this case Kirkpatrick's equation (1) should be replaced by the expression

$$P = \frac{1 - K\cos^2 2\theta \cos^2 2\phi}{K - \cos^2 2\theta \cos^2 2\phi}$$

where θ is the glancing angle for the crystal C_1 and ϕ is the same angle for crystal C_2.



For ten per cent polarization, $K = 1.06$, and for a five per cent polarization $K = 1.032$. Hence the method is easily capable of detecting a five per cent polarization.

The apparatus used is shown in figure 1. A water-cooled molybdenum tube was mounted so it could be rotated through ninety degrees. The

rays were rendered monochromatic by reflection from a calcite crystal C_1. The beam was collimated by slits S_1 and S_2 which were about 0.5 × 10 mm. A lead plate S was placed as shown to keep any general radiation from reaching S_2. A rock salt crystal C_2, ground parallel to the (100) plane, was mounted on the table of a Bragg spectrometer. The intensity measurements were made with an ionization chamber and a Compton electrometer, having a sensitivity of about 4000 mm./volt. The sector disk was used in reducing the intensity of the incident beam while determining the value of I.

With the tube initially in the horizontal position, the calcite crystal C_1 was adjusted to give the first order reflection of the K_α lines. Care was taken that the whole beam passing through slit S_2 was intercepted by the rock salt crystal C_2. The crystal C_2 and the ionization chamber were adjusted to give the fourth-order reflection. The slit S_3 was opened wide enough to admit into the ionization chamber all the rays reflected by the crystal C_2. The total deflection of the electrometer as the crystal is rotated with uniform angular velocity gives the value of E in the quantity $E\omega/I$. After making determinations of E the crystal was removed, and the ionization chamber was placed to receive the beam reflected directly from crystal C_1, which now passed through the rotating sector disk. The rate of deflection of the electrometer was taken as a measure of I. A number of these readings were made and the value of $E\omega/I$ calculated. The tube was then turned to the vertical position and the procedure repeated. The values of $E\omega/I$ thus determined are expressed in arbitrary units in the following table.

TABLE 1

TUBE HOR.	TUBE VERT.	TUBE HOR.	TUBE VERT.	TUBE HOR.	TUBE VERT.	TUBE HOR.	TUBE VERT.
17.53	17.00	16.50	17.48	15.60	15.35	15.27	14.95
16.96	17.38	16.50	17.15	15.25	15.35	14.90	14.98
18.05	17.30	17.75	17.60	15.70	15.25	14.65	15.50
16.85	17.51	16.40	16.95		15.75	15.30	15.22
17.46		17.15					
17.36	17.30	16.86	17.29	15.51	15.43	15.03	15.16

Average for the horizontal position = 16.19.
Average for the vertical position = 16.29.
From which $K = 1.006$
and $P = 0.992$

The above value of P differs from unity by an amount within the probable experimental error. Hence the result of this experiment indicates that the K_α lines of molybdenum are not polarized in excess of one per cent.

While this work was in progress, J. A. Bearden[5] had published his results on the same problem. Although his method is different, his results are in agreement with those of the author.

In conclusion the author wishes to express his appreciation to Professor A. H. Compton and Mr. J. A. Bearden for the suggestion of the problem and for the assistance which they have given.

[1] O. G. Barkla, *Nature*, **71**, 477, 1905.
[2] J. B. Bishop, *Phys. Rev.*, **28**, 625, 1926.
[3] R. J. Havighurst, *Phys. Rev.*, **31**, 16, 1928.
[4] Paul Kirkpatrick, *Phys. Rev.*, **29**, 632, 1927.
[5] J. A. Bearden, *Proc. Nat. Acad. Sci.*, June 11, 1928.

THE ORIGIN OF THE CONTINUOUS SPECTRUM OF THE HYDROGEN MOLECULE

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Communicated September 24, 1928

The continuous spectrum of the hydrogen molecule extends from the extreme ultra-violet far into the visible part of the spectrum. A theoretical discussion of the experimental facts, as found by Blackett and Franck, Oldenberg, Horton and Davies, Crew and Hulbert, and others, is given by J. Kaplan. The most successful explanation was the theory that this continuous spectrum originates in the dissociation of a hydrogen molecule having electronic (and perhaps vibrational) energy into two atoms having various amounts of relative kinetic energy.[1]

The application of wave mechanics by Heitler and London[2] to calculate the potential energy curves of the ground state of H_2 completes the system of electronic levels in an interesting way. They find besides the known 1^1S state another curve without any minimum, representing another way in which two H atoms may react with each other. They call this curve 1^3S, because the symmetry relations between the two electrons suggest this designation. Figure 1 shows the curve 1^3S as calculated by Y. Sugiura.[2] The curve 1^1S represents the experimental value of the approximated potential energy curve for 1^1S. It differs about 1.5 volts at the minimum from the calculated 1^1S curve, but has the same shape. We draw in figure 1 the parabolic approximation of the minimum of the potential energy curves belonging to the 2^3S state. Figure 2 shows the picture of the electronic levels as given by Birge,[3] completed by the 1^3S level, whose nuclear motions are not quantized, and which corresponds to the curve in figure 1. The transitions between the singlet levels were analyzed by Richardson in the visible and by Dieke and Hopfield and Hori in the ultra-violet. The triplet system has been arranged by Richardson.[3] No intersystem combinations are known. We have regarded the non-desig-

nated C level as in the singlet system, because only combinations of it with singlet terms are known.

As the 1^3S is 4.35 volts higher, the dissociation energy of H_2, than 1^1S, one can compute its Rydberg demoninator. One obtains the following table for the Rydberg denominators and their differences for the singlet and triplet S-terms of H_2 and He:

	TRIPLET			SINGLET		
	H_2		He	H_2		He
$1S$	1.1095		(Pauli "Verbot")	0.9396		0.74
		0.8242	...		0.8524	1.105
$2S$	1.9337		1.889	1.7920		1.842
		1.0924	0.806		...	0.937
$3S$	2.9261		2.695	?		2.779

That the denominator of the 1^3S is 1.1095 and not 1.0000, as one would expect on the first view, because it is the same electronic level as the Bohr 1_1 orbit, is due to the difference in ionization potential of H_2 and H.

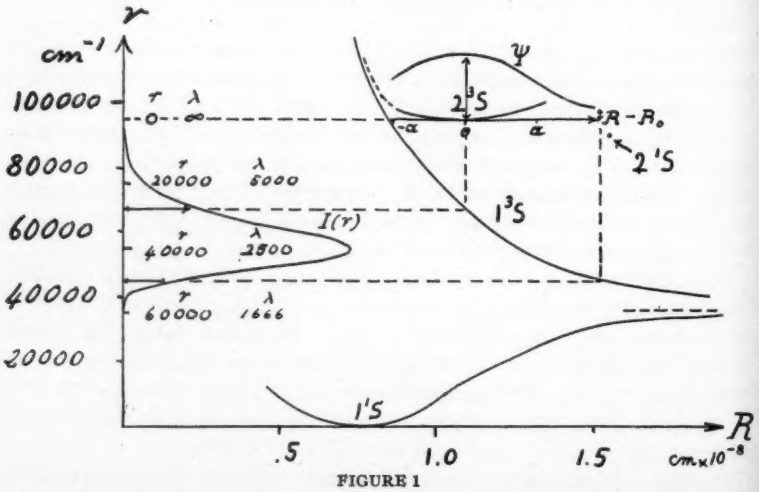

FIGURE 1

1^1S, 1^3S, 2^3S: potential energy (ν expressed in frequency units) of these states as function of the nuclear separation R for H_2. ψ : "Eigenfunction" of the zero vibration level of 2^3S as function of $R - R_0$ (R_0 being the equilibrium separation). *a:* See formula 2. I(ν): Intensity of continuous spectrum $2^3S \rightarrow 1^3S$ as function of the emitted frequency ν, of wave-length λ.

The continuous spectrum finds in our diagram (figure 2) a very natural explanation: The transition from any one of the excited triplet levels to the ground state of this system (1^3S) must give a continuous spectrum extending from the extreme ultra-violet into the visible.

Applying the principle of Condon,[4] which is the wave mechanics analogue

of the one stated by Franck,[5] that such transitions are the most probable to occur, in which position and momentum of the nuclei change least, the curve I(ν) in figure 1 has been drawn. The curve is obtained by forming the matrix elements of the transition probabilities

$$P(e'n',e''n'') = \int P(x,R).\psi_{el}(e',x).\psi_{vib}(e'n',R)\psi_{el}(e'',x).\psi_{vib}(e''n'',R).dx.dR,$$

where $P(x,R)$ represents the electrical momentum of the molecule as a function of the electronic coördinates x and the nuclear separation R, e and n being the respective quantum numbers of the electronic and vibra-

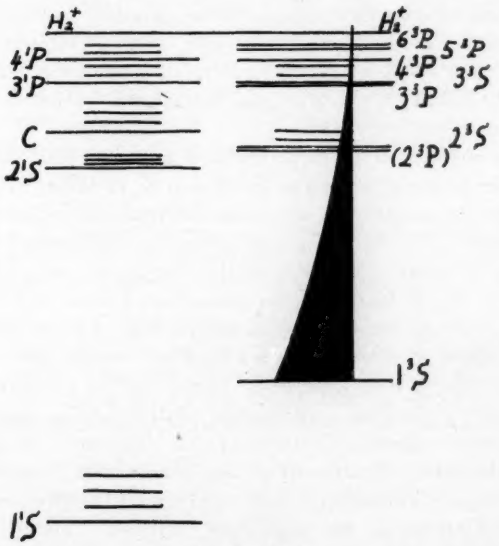

FIGURE 2

Term arrangement of H_2: Electronic levels, long dashes, vibrational levels, short dashes. The non-quantized levels of nuclear motions of 1^3S are drawn as a continuum of states.

tional states. Condon showed, that after integrating over the electronic coördinates x, we obtain a function $P'(e'e'',R)$ of R only, which probably can be treated as constant in the range, which contributes most to the value of the integral; therefore

$$P(e'n', e''n'') = \int P'(e'e'',R).\psi_{vib}(e'n',R).\psi_{vib}(e''n'',R).dR = P'(e'e'',R_0)\int \psi_{vib}(e'n',R).\psi_{vib}(e''n'',R).dR \quad (1)$$

In the particular problem, where n'' represents the continuous set of nuclear motion energies of 1^3S, one can estimate the above integral by reflecting the Eigenfunction $\psi_{vib}(e'n',R)$ of the lowest vibration level of 2^3S ($e' = 2$,

$n' = 0$) on the potential energy curve $R = R(\nu)$ of 1^3S. Regarding the vibratory motion as harmonic, $\psi_{vib}(2O,R)$ becomes:

$$\psi_{vib}(2O,R) = \text{const } e^{-\frac{1}{2}\left(\frac{R}{a}\right)^2} \tag{2}$$

where a has the value

$$a = \sqrt{\frac{h}{4\pi^2 c \cdot \omega\mu}}. \tag{3}$$

The reflection gives $\psi'(\nu) = \psi(R(\nu))$, and $I(\nu) = \gamma^4\psi'(\nu)^2$ is therefor proportional to the spectral intensity. This is of course a very rough approximation, as only the elements of the parabolic approximation were known. But it shows clearly, that with a small excitation potential (lowest vibration level) we get the maximum intensity in the ultra-violet part,[6] and the end of the spectrum near 60,000 cm.$^{-1}$ (1700 Å) as found by Hopfield and Lewis and others.[1]

Oldenberg[1] excited H_2 in the presence of argon to limit the electron at the resonance potential of argon (11.57 and 11.77 volts) in order to get only the continuous spectrum which extends from the end of the $2^1S \longrightarrow 1^1S$ band system (11.1 volts for lowest vibration level) toward longer wavelength with 0.47, resp., 0.67 volt available for kinetic energy of the separating atoms. But he found only the bands and no trace of any continuous spectrum. Applying the Franck-Condon principle here again we see that such a continuous spectrum could not originate because the eigenfunction of a particle moving with appreciable kinetic energy along the horizontal part of 1^1S would oscillate very rapidly relative to the eigenfunctions of any of the lower vibrational states of 2^1S (because a is very long on account of the small vibration frequency of this state; formula (2) gives 0.39×10^{-8} cm.). The integral, formula (1), must therefore vanish rapidly as the kinetic energy in the final state increases. The Heisenberg indetermination principle gives an estimate how far such a continuous spectrum would extend: Identifying in

$$\Delta q . \Delta p = \frac{h}{2\pi}$$

a with Δq, we find that the approximate extent of the continuous spectrum of $2^1S \longrightarrow 1^1S$ is 0.04 volt (350 cm.$^{-1}$ or 8 A.U. at $\lambda = 1700$).

To excite the continuous spectrum $2^3S \longrightarrow 1^3S$ (or $2^3P \longrightarrow 1^3S$, which is nearly the same energy) we need 11.7 volts.[3]

Witmer[7] in his experiments finds that the first resonance potential of argon (11.57 volts) does not limit the electron velocity wholly, because his plate (figure 1, p. 1224) shows the other resonance line (11.78 volt) in considerable intensity. But there were no lines of higher excitation potentials found. He draws an estimated distribution of electron velocities (figure 2 in his paper), where 11.57 cuts down the number of elec-

trons to about $^1/_2$, and 11.78 takes away practically the other half. It may be that the number of electrons, whose speed is higher than the lower resonance potential 11.57, is less than $^1/_2$. However, it is certain that there is still a considerable number of electrons with speeds between 11.57 and 11.77 volts. The fact that no continuous spectrum appears suggests that the terms of the triplet system lie about 0.1 volt higher relative to the singlet system than the values given by Birge.[3] As no intersystem combinations are known the value of the triplet terms relative to 1^1S are calculated by the extrapolations ($m = \infty$) of the Ritz formula for the series 2^1S-m^1P and 2^3S-m^3P. The extrapolation of the later series, where bands for $m = 3, 4, 5, 6, 7$ and 8 are known, is probably very accurate. The extrapolation of the singlet system, however, is less certain as only bands for $m = 3$ and 4, and a few lines probably belonging to $m = 5$, are known.

In conclusion we wish to express our thanks to Prof. E. U. Condon for his very helpful suggestions.

* NATIONAL RESEARCH FELLOW.

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[2] W. Heitler and F. London, *Zeits. Physik*, **44**, 455, 1927; Y. Sugiura, *Ibid.*, **45**, 484, 1927.

[3] R. T. Birge, *Proc. Nat. Acad. Sci.*, **14**, 12, 1928.

[4] E. U. Condon, *Physic. Rev.*, **28**, 1182, 1926; *Proc. Nat. Acad. Sci.*, **13**, 462, 1927. A detailed discussion of the wave mechanical interpretations of this theory as used here is to be given soon in the *Physical Review*. For the opportunity of seeing the manuscript and conversations on the subject of this paper, we wish to express our thanks to Prof. Condon.

[5] J. Franck, *Trans. Far. Soc.*, **21**, part 3, 1925.

[6] J. Stark, M. Goercke u. M. Arndt, *Ann. Physik*, **54**, 69, 1917.

[7] W. Witmer, *Physic. Rev.*, **28**, 1223, 1926.

THE CRITICAL POTENTIALS OF MOLECULAR HYDROGEN

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Out of a number of experiments in recent years on the impact of electrons with hydrogen molecules, there come certain results which at first sight appear discordant. On the one hand the experiments on ionization show that an electron, when it ionizes a hydrogen molecule, does so without causing dissociation. That is, the production of atomic ions as the primary result of impact of moderate speed electrons with hydrogen molecules is a process which occurs rarely if at all. On the other hand,

dissociation into uncharged atoms by electrons with velocities both below and above the ionizing potential, does occur frequently. There is therefore an apparent inconsistency, but the writers believe it is explained by theoretical considerations similar to those advanced by Winans and Stueckelberg[1] in the preceding paper. In fact almost all the critical potential data on hydrogen now seem to fit in the theoretical scheme. However, before presenting the theory, a more precise summary of the experimental results will be given.

Suppose we present the experimental observations as a function of the speed of the impacting electrons. If diatomic hydrogen be bombarded by electrons of any speed below eleven volts the electrons lose a small indeterminate amount of energy; that is, the collisions are not perfectly elastic as in the rare gases, but are very nearly so. No effect of radiation or dissociation is observed. As the speed of the electrons is increased up to twelve volts several effects[2] are observed, first inelastic impact,[3] second radiation photoelectrically effective,[4] third the production of atomic hydrogen (or at least of some form of hydrogen that "cleans up" and is chemically active[4,5]). The exact critical potentials where these processes begin to occur are not very precisely determined but are all in the neighborhood of 11.5 volts.

Now, if the speed of the electrons is further increased the experimental evidence is less definite. Apparently radiation becomes more intense, possibly with discontinuities corresponding to higher critical potentials. In particular a number of investigators report an increase in radiation at about 12.8 volts. As to the production of atoms, that also appears to increase. Thus, Glockler, Baxter and Dalton[5] state that the effectiveness of the impacting electrons increases rapidly between 11.4 volts and the molecular ionizing potential above which the change is slow. Experiments on inelastic impact give no definite results in this region.

When the electrons reach a speed of 13.5 volts, the ionizing potential of atomic hydrogen, weak ionization is always observed, indicating that there is always some atomic hydrogen present. In the past this has been explained by dissociation due to the hot filament.

Somewhat above this voltage but before the molecular ionization potential, are a group of radiating potentials observed by Olsen and Glockler but in no other experiments.

Then at about 15.9 volts strong ionization sets in, which has been shown to be ionization without dissociation. Furthermore, no evidence has been found at this or any higher voltage of the formation of atomic ions from molecules as the immediate result of an electron impact. However, such a process may occur if of very small probability, since it might be masked by the large number of atomic ions formed by secondary dissociation of the molecular ions. This latter process occurs only if the molecular ions

have acquired a certain minimum kinetic energy before they make collisions. (See Dorsch and Kallmann, *Zs. Phys.*, **44**, p. 543, 1927.)

As the speed of the impacting electrons is still further increased no new processes are observed by the positive ray or "clean-up" methods. Some experimenters have observed additional ionization setting in at about thirty volts. Of more importance, however, are the results of Franck and Blackett, who showed that the emission of Balmer lines was a primary result of impact of thirty volt or higher speed electrons. In other words, they showed dissociation may occur with excitation of one (or perhaps both) atoms.

We may summarize the principal results in tabular form as given below.

	PROCESS	MINIMUM ENERGY REQUIRED	REMARKS
(*a*)	$H_2 \longrightarrow H + H$ Radiation produced	11.5	
(*b*)	More radiation	12.8	Not very definite
(*c*)	$H_2 \longrightarrow H_2^+ + e$	15.9	The usual ionization
(*d*)	$H_2 \longrightarrow H^+ + H + e$		Does not occur
(*e*)	$H_2 \longrightarrow H' + H$(or H')	30	

It should be pointed out that we have little evidence as to the relative probabilities of these processes at different voltages, though from the small number of atomic ions observed at low pressures we may infer that (*a*) is improbable compared to (*b*) at potentials above 15.9.

In order to interpret these phenomena in terms of energy levels and potential energy curves we will need not only those given in the previous paper but also the potential energy curve for the normal state of the hydrogen molecular ion. This has been calculated by Burrau.[6] In the figure a curve drawn from his data is given. To it have been added a curve for the 2^1S from band spectra data and the curves given by Winans and Stueckelberg for the 1^3S and 2^3S states.

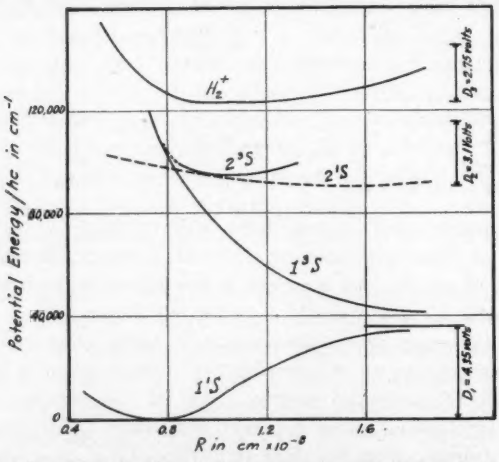
Consider the possible effect of an electron impact on an H_2 molecule. If the electron has less than 11 volts the only possible transition it may cause is to the 1^3S state. But applying the Franck-Condon principle we see that the probability of such a transition will be small except for those nuclear separations where the 1^3S curve nearly coincides with that for the 2^3S term. In other words we might expect a little but only a little atomic hydrogen to be produced below eleven volts since the 1^3S state is unstable.

Slightly above eleven volts the excitation to the 2^1S state becomes possible. Although the nuclear binding in this state is considerably weaker than in the normal state and the curve suggests the possibility of dissociation on excitation to this state, the intensity distribution in the absorption bands indicates that this is not usually the case.[7] Return from this state to the normal would, of course, produce radiation that would be photoelectrically effective.

Electrons of somewhat greater speed might do any of three things, (1) excite directly to the 1^3S state producing hydrogen atoms with big kinetic energy, (2) excite to the 2^1S state producing radiation, (3) excite to the 2^3S state which would then revert to the 1^3S state giving off the continuous spectrum and producing atomic hydrogen simultaneously.

The writers believe that some or all of these three processes occur in the various experiments which find a critical potential at about 11.5 both for the production of radiation and of atomic hydrogen.

If the speed of the electrons be still further increased the possibilities become more and more numerous. We may suggest the correlation of



The curves in the above figure represent the potential energy as a function of nuclear separation for five different electronic states of the hydrogen molecule. The values given at the right for the heats of dissociation are obtained from band spectra for 1^1S and 2^1S states and from Burrau's paper for the ion. They indicate the heights which the curves would approach if extended to the right.

the 12.8 radiating potential with the "C" level but the uncertainties of both theory and experiments make further correlations futile. Two points remain to be mentioned for this region of velocities. First, we may expect more and more atomic hydrogen to be produced by excitation to higher triplet levels and reversion to the 1^3S. Second, the presence of this atomic hydrogen probably explains the atomic critical potentials which are so often observed.

Finally, suppose the electrons have sufficient velocity to ionize the molecule, that is to change it from the lowest to the topmost curve in our figure. If we compare the shapes of the two curves and positions of

their minima, we see at once that the most probable transitions are going to give nuclear separations which will not result in dissociation. This is in perfect accord with experiment.

Until we know more of the excited states of the H_2^+ ion we cannot proceed with explanations of the effects that still faster electrons may produce.

[1] Winans and Stueckelberg, these PROCEEDINGS, **14**, 867, 1928.

[2] We are assuming the weak ionization sometimes reported at about 11 volts, is due to an impurity.

[3] Compton and Mohler, *Critical Potentials*, p. 115.

[4] Hughes and Skellet, *Physic. Rev.*, **30**, pp. 11–35, 1927.

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[6] Burrau, *Kgl. Danske Vid. Selskal. Math-fys. Med.*, **7**, 14, 1927.

[7] Hopfield, *Physic. Rev.*, **31**, p. 918, 1928.

THE STRUCTURE OF THE COMPTON SHIFTED LINE

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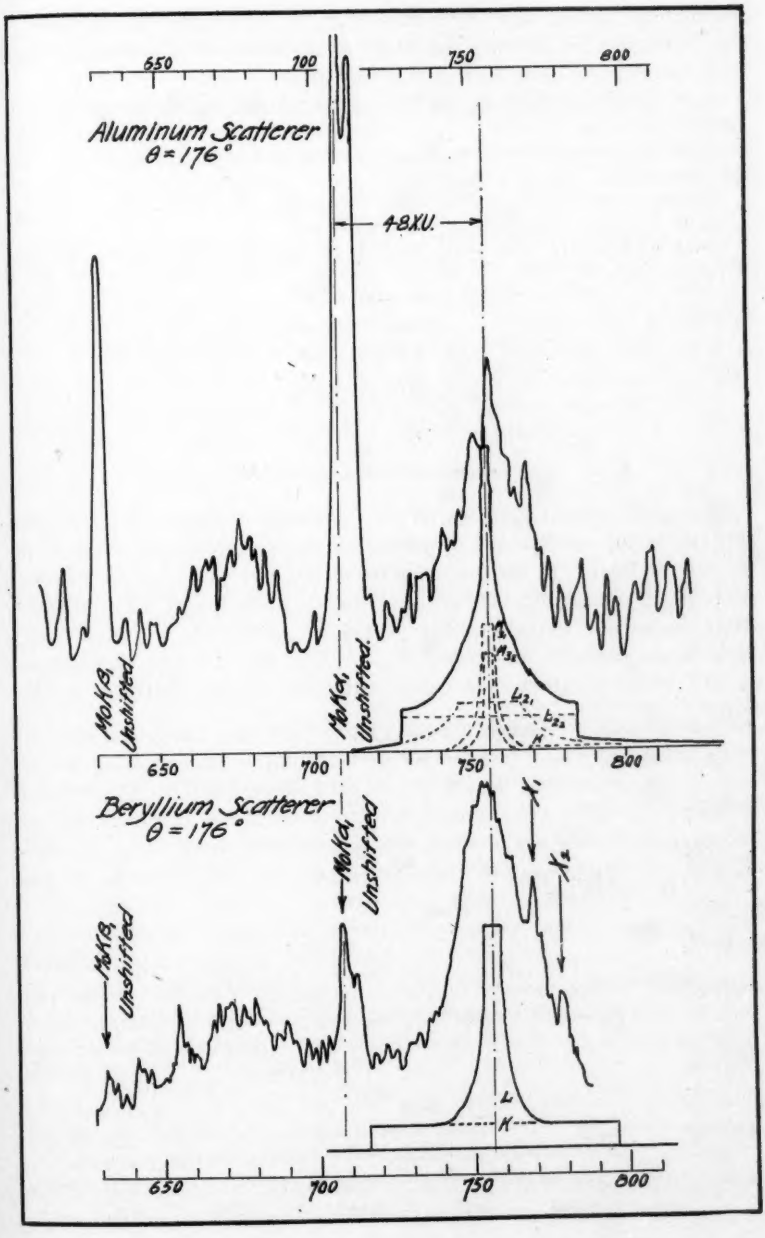
According to Wentzel's[1] wave mechanical theory of modified x-ray scattering and also according to Jauncey's[2] classical-quantum theory of the same effect (though not explicitly so stated by Jauncey), the modified scattered x-radiation is regarded as due to many Smekal transitions[3] in each of which the initial state of the electron is a discrete negative energy level and the final state is one of the continuum of positive energy levels. In both of these theories the shifted "line" is predicted as a diffuse band, the diffuseness being due to the momenta of bound electrons in the dynamic atom model. Indeed, the natural breadth of the Compton modified line can be regarded as a Doppler broadening for x-rays scattered by moving electrons in much the same way as the temperature broadening is regarded in the case of optical spectra. The broadening of the Compton line is the most direct evidence for a dynamic atom model yet found. The structure of the line can be interpreted in such a way as to give the probability distribution of electron momenta in atoms. The breadth for circular orbits should be proportional to the effective atomic number of the scatterer.

In order to determine the natural structure of the Compton modified line it is necessary to first minimize an experimental cause for the breadth of the line which is ordinarily superposed upon the natural breadth so as to mask the latter. This cause is the unavoidable inhomogeneity of scattering angle. The x-radiation incident upon the scattering material

must be somewhat divergent, for the more divergent the cone of incident x-rays the more primary energy available for the very wasteful scattering process. The scattered x-rays must be sensibly parallel if they are to be analyzed spectroscopically by a crystal. Hence the unavoidable inhomogeneity of scattering angle. There results a corresponding inhomogeneity of shift since the shift is related to scattering angle by the formula $\lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta)$. A minimum inhomogeneity of shift due to inhomogeneity of scattering angle occurs when θ, the scattering angle is in the vicinity of 180° where the expression above has an analytic maximum. Scattering at 180° presents, moreover, the advantage of a maximum shift. Also the predicted natural breadth of line is a maximum for 180° scattering angle.

To facilitate scattering at this large angle and also to permit bringing the scattering material close to the source of primary x-rays so as to increase incident intensities and reduce the necessarily rather long exposure time, a special tube[4] was constructed containing the scattering material and the Seeman crystal spectrograph in a small box supported on the end of the standard Coolidge water-cooled molybdenum target. The primary radiation leaves the target at a small angle to its surface and the scattered radiation returns in a line parallel to that surface about a millimeter away. The scattering angles vary from 170° to 178°, a large proportion of scattering being at 176°. The increase in the natural line breadth should be less than 1 X.U. Great care was taken in designing the geometry of the box to avoid observing any radiation other than that coming from the scattering block. The analyzing crystal was a tiny piece of quartz (used for its heat-resisting properties). The resolution of the spectrograms is good as can be seen by the width of lines other than the Compton line. An analysis of some of the negatives with the microphotometer yielded the experimental curves shown. The theoretical curves were computed with the help of Jauncey's theory and reasonable assumptions as to electron-momentum distribution.

The correspondence between observed and calculated line structure for scattering by aluminum ($Z = 13$) is good. However, the experimentally found distribution for beryllium ($Z = 4$) is wider than theory predicts. Two faint but perfectly distinct lines also appear of wave-lengths 768 and 777 X.U. The shift of these lines is too great to account for them as Smekal transitions between discrete energy levels in beryllium. Neither have they yet been accounted for as characteristic fluorescence lines of any element whatever. The possibility of accounting for the extra breadth of the shifted line by double scattering considerations is now being investigated. The work is being continued both by the double crystal method of Bergen Davis[5] and by means of a special newly devised multiple crystal


650
700
750
800
Aluminum Scatterer
θ = 176°
48 X.U.
Mo Kβ, Unshifted
Mo Kα, Unshifted
Beryllium Scatterer
θ = 176°
Mo Kβ, Unshifted
Mo Kα, Unshifted
K
L
K_1
K_2

spectrograph having some of the advantages of the concave optical grating. The latter method permits the study of scattering at other angles than 180°, maintaining good homogeneity of scattering angle.

[1] G. Wentzel, *Zeits. Phys.*, **43**, 1–2, pp. 1–8, 1927; *Ibid.*, **43**, 11–12, pp. 779–787, 1927.

[2] J. E. M. Jauncey, *Phys. Rev.*, **25**, pp. 314–322, Mar., 1925; *Ibid.*, **25**, pp. 723–736, June, 1925.

[3] Smekal, *Naturwiss.*, **11**, pp. 873, 1923. *Zeits. Phys.*, **32**, pp. 241, 1925.

[4] J. W. DuMond, *Nature*, **116**, p. 937, Dec., 1925.

[5] Bergen Davis, *Proc. Nat. Acad. Sci.*, **13**, pp. 419, June, 1927. *Phys. Rev.*, pp. 331, Sept., 1928.

SOME MULTIPLETS OF DOUBLY IONIZED LEAD

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The most conspicuous lines in the spectrum of doubly ionized lead (Pb III) would be expected to arise from singlet and triplet terms as in the case of Hg I. In the normal state of the Pb^{++} ion the two valence electrons are presumably in 6*s* orbits giving rise to the lowest term $(6s6s)^1S_0$. Other important terms to be expected are $(6s6p)^3P_{0,1,2}$, $(6s6d)^3D_{1,2,3}$, $(6s6f)^3F_{2,3,4}$, $(6s7s)^3S_1$ and $(6p6p)^3\overline{P}_{0,1,2}$. The singlet terms are omitted as this communication deals only with combinations between triplet terms.

TABLE 1

TRIPLET SYSTEM OF PB III

	$(6s6p)^3P_0$		$(6s6p)^3P_1$		$(6s6p)^3P_2$
$(6p6p)^3\overline{P}_0$			1279.44 (15)		
			78159		
			7535		
$(6p6p)^3\overline{P}_1$	1114.99 (9)		1166.94 (15)		1406.57 (12)
	89687	3993	85694	14599	71095
			14734		14738
$(6p6p)^3\overline{P}_2$			995.75 (10)		1165.05 (15)
			100428	14595	85833
$(6s6d)^3D_1$	1030.44 (15)		1074.63 (15)		1274.56 (10)
	97046	3991	93055	14597	78458
			477		482
$(6s6d)^3D_2$			1069.15 (20)		1266.79 (15)
			93532	14592	78940
					1032
$(6s6d)^3D_3$					1250.43 (20)
					79972
$(6s7s)^3S_1$	1052.23 (7)		1098.39 (10)		1308.10 (15)
	95036	3994	91042	14595	76447

A search was first made for the characteristic group ^3P-$^3\overline{P}$ which is usually strong in the spectrum of an atom with two valence electrons. On referring to the wave-length measures of Carroll[1] of the hot spark in the Schumann region and to some unpublished measures made by Dr. R. J. Lang in the same region the ^3P-$^3\overline{P}$ and ^3P-^3D combinations were found to appear with considerable intensity. These combinations together with $(6s6p)^3P$-$(6s7s)^3S$ are given in table 1, Lang's measures being quoted.

A search was then made for the fundamental combination ^3D-^3F, using measures made by the author[2] in the hot vacuum spark for the region 2300 Å to 5000 Å. An outstanding triplet of lines λλ 3043.92, 3137.92, 3176.61 belongs to this combination. These lines were attributed to Pb III by Kimura and Nakamura[3] and have been mentioned by Rao and Narayan[4] as probably forming part of a ^3D-^3F combination. The complete group is as follows, the wave-lengths being given as λIA air.

TABLE 2

FUNDAMENTAL TRIPLET OF PB III

	$(6s6d)^3D_1$		$(6s6d)^3D_2$		$(6s6d)^3D_3$	
$(6s6f)^3F_3$			3137.92 (10)		3242.86	(5)
			31859.0	1030.9	30828.1	
			502.9		502.1	
$(6s6f)^3F_2$	3043.92 (10)		3089.16 (6)		3190.89	(0)
	32842.8	480.9	32361.9	1031.7	31330.2	
					140.8	
$(6s6f)^3F_4$					3176.61	(10)
					31471.0	

It will be noticed that the ^3F terms are abnormal, $^3F_3$ being lower than $^3F_2$. It is also interesting to observe that Carroll[1] gave two alternative choices for the diffuse triplet of Pb IV and that in the first of these occurs the line λ 1069.15 which has here been identified as $(6s6p)^3P_1$-$(6s6d)^3D_2$ of Pb III. Not much progress has been made in the identification of the singlet spectrum. However, it is probable that λ 1048.86 is $(6s6s)^1S_0 - (6s6p)^1P_1$.

An attempt is being made to identify further multiplets which will enable the term values to be deduced.

The author wishes to express his thanks to Dr. R. J. Lang for the use of his wave-length measures in the Schumann region and to acknowledge a grant from the Research Council of Canada which was of assistance in this work.

[1] Carroll, J. A., *Phil. Trans. Roy. Soc.*, **A225**, 357–420, 1925.
[2] Smith, S., *Proc. Roy. Soc. Canada*, **1928** (in press).
[3] Kimura, M., and Nakamura, G., *Jap. J. Phys.*, **3**, 197–215, 1924.
[4] Rao, K. R., and Narayan, A. L., *Proc. Roy. Soc.*, **A119**, 607–627, 1928.

SPECTRAL INTENSITIES OF RADIATION FROM NON-HARMONIC AND APERIODIC SYSTEMS

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In order to find expressions for the spectral intensities and the spatial distribution of radiation from the most general kind of quantum dynamical system, it is necessary to find the matrix components of the components of acceleration of the system. These can easily be found in the following way. We have, if A is the acceleration in the X_k direction and H is the total energy,

$$A_k = \dot{v}_k = -\frac{1}{ih}(v_kH - Hv_k) \tag{1}$$

$$v_k = \dot{X}_k = -\frac{1}{ih}(X_kH - HX_k) \tag{2}$$

which give

$$h^2A_k = 2HX_kH - X_kH^2 - H^2X_k. \tag{3}$$

If $H = T + V$ where T is the kinetic energy and V the potential energy, then

$$h^2A_k = 2TX_kT - X_kT^2 - T^2X_k - X_kV^2 - V^2X_k + 2VX_kV + 2TX_kV + 2VX_kT - X_kTV - TVX_k - X_kVT - VTX_k. \tag{4}$$

If V does not contain the X_k-component of velocity explicitly, V and X_k commute and (4) then reduces to

$$h^2A_k = 2TX_kT - X_kT^2 - T^2X_k + TX_kV + VX_kT - X_kTV - VTX_k. \tag{5}$$

If $T = \frac{1}{2m}(P_1^2 + P_2^2 + P_3^2) = -\frac{h^2}{2m}\nabla^2$ then as $\nabla^2X = X\nabla^2 + 2\frac{\partial}{\partial x}$, $\nabla^4X = X\nabla^4 + 4\frac{\partial}{\partial x}\nabla^2$, $\nabla^2X\nabla^2 = X\nabla^4 + 2\frac{\partial}{\partial x}\nabla^2$, the sum of the first three terms on the right-hand side of (5) vanish. When (5) is completely reduced it gives

$$A_k = -\frac{1}{m}\frac{\partial V}{\partial X_k} \tag{6}$$

a result which might have been expected in the first place. Then the matrix components of the acceleration in the X_k direction are given by

$$A_k(r,s) = -\frac{1}{m}\int \frac{\partial V}{\partial x_k}\psi_r^*\psi_s dq \tag{7}$$

where the integration is performed over coördinate space. This general formula can apply to any system where the potential energy does not involve X and the kinetic energy is $\frac{1}{2m}(P_1^2 + P_2^2 + P_3^2)$. Let $A = (A_1^2 + A_2^2 + A_3^2)^{1/2}$ be the resultant acceleration. If the potential energy does not involve any of the velocities, then the matrix components of A are given by

$$A(r,s) = -\frac{1}{m}\int\left[\left(\frac{\partial V}{\partial x_1}\right)^2 + \left(\frac{\partial V}{\partial x_2}\right)^2 + \left(\frac{\partial V}{\partial x_3}\right)^2\right]^{1/2} \psi_r^* \psi_s dq. \quad (8)$$

Classically an electron with resultant acceleration A radiates energy at the rate $\frac{2e^2A^2}{3C^2}$ so that it should be expected that the total energy radiated by r,s quantum jumps should be

$$P(r,s) = \frac{2e^2}{3m^2c^2}\left|\int\left[\left(\frac{\partial V}{\partial x_1}\right)^2 + \left(\frac{\partial V}{\partial x_2}\right) + \left(\frac{\partial V}{\partial x_3}\right)^2\right]^{1/2} \psi_r^* \psi_s dq\right|^2. \quad (9)$$

Also, classically, the intensity of radiation in a direction making an angle θ with the resultant acceleration is, in the case of slow velocities,

$$I = \frac{A^2e^2\sin^2\theta}{4\pi r^2c^3}. \quad (10)$$

Let l_1, l_2, l_3 be the direction cosines of the direction in which the intensity is desired. Then (10) can be rewritten classically as

$$I_{l_1,l_2,l_3} = \frac{e^2}{4\pi r^2c^3}[A^2 - (l_1A_1 + l_2A_2 + l_3A_3)^2]. \quad (11)$$

Then as $l_1A_1(r,s) + l_2A_2(r,s) + l_3A_3(r,s) = -\frac{1}{m}\int\left[l_1\frac{\partial V}{\partial x_1} + l_2\frac{\partial V}{\partial x_2} + l_3\frac{\partial V}{\partial x_3}\right]\psi_r^*\psi_s dq$, we have for the intensity in the l_1, l_2, l_3 direction of radiation from r,s jumps

$$I_{l_1,l_2,l_3}(r,s) = \frac{e^2}{4\pi m^2c^3r^2}\left\{\left|\int\left[\left(\frac{\partial V}{\partial x_1}\right)^2 + \left(\frac{\partial V}{\partial x_2}\right)^2 + \left(\frac{\partial V}{\partial x_3}\right)^2\right]^{1/2}\psi_r^*\psi_s\right|^2 - \left|\int\left[l_1\frac{\partial V}{\partial x_1} + l_2\frac{\partial V}{\partial x_2} + l_3\frac{\partial V}{\partial x_3}\right]\psi_r^*\psi_s dq\right|^2\right\}. \quad (12)$$

In a uniform field of force F along the X-axis where $V = eFX$, then from (7) $A_1(r,s) = 0$ when $r \neq s$ so that A_1 is a diagonal matrix as we should expect, as it is a constant of the motion. Then from (9) it is seen that a uniformly accelerated electron abstracts a constant stream of energy from the field so that the spectrum consists of a single line of zero frequency.

For a hydrogen-like atom of nuclear charge Z the potential energy is $V = -eZ/r$ and $\frac{\partial V}{\partial z} = eZ \cos\theta/r^2$. When the wave equation is separated in spherical polar coördinates so that the unnormalized wave functions are given by

$$\psi_{n,l,m}(r,\theta,\phi) = x(r)e^{im\phi}P_l^m(\cos\theta)$$

where

$$x(r) = \left(\frac{2r}{a_0 n}\right)^l \cdot e^{-r/a_0 n} L_{l+n}^{2l+1}\left(\frac{2r}{a_0 n}\right)$$

and where $a_0 = h^2/4\pi^2 meZ$, we get from (7) and results assembled by Kupper*

$$A_3(n,l,m;n',l',m') = -\frac{eZ}{m}\left(\frac{l^2-m^2}{4l^2-1}\right)^{1/3} \cdot \frac{1}{N_r}\int_0^\infty x_n(r)x_{n'}(r)dr \quad (13)$$

where N_r is a normalizing factor. The factor of this expression depending on n,n' differs from that which would be obtained by the Heisenberg amplitude rule. The latter rule is only strictly accurate when applied to an harmonic oscillator.

* *Ann. Physik*, **86**, 511, 1928.

THE AURORA RED LINE

By Joseph Kaplan

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Recently[1] the author reported some experiments concerning the excitation of the aurora green line when oxygen was mixed with active nitrogen. In that report it was mentioned that a red line having a wave-length of 6654.8 A.U. was also excited and its agreement with an unclassified oxygen line prompted the suggestion that the line 6654.8 may be an oxygen line. One would therefore be justified in concluding that this line should be observed in the light of the night sky and in the Aurora Borealis.

Following a suggestion by Dr. G. Cario, the author reëxamined the plates on which the red line was photographed and the conclusion has been reached that this "line" is in reality a band belonging to the first positive group of nitrogen. In the following discussion the reasons for this conclusion will be presented.

While studying the conditions under which the green line was excited it was noted that the red line diminished in intensity very little, as the

amount of oxygen was reduced. Because of this it was doubtful whether or not this line should be assigned to oxygen. It was difficult, however, to call it an α-band since each of the other bands in the afterglow consisted of four heads, whereas this would have been an α-band with a single head. A photograph of the discharge tube spectrum in this region showed only the usual four-headed bands, and did not show this line at all. Consequently, it seemed reasonable at the time to assign the line to oxygen, especially in view of the remarkable agreement in wave-length between it and the unclassified line of oxygen at 6654.8 A.U.

Using the data presented by A. H. Poetker[2] it is possible to predict the positions of α-bands corresponding to transitions that are normally very weak in the discharge tube. In active nitrogen, many of the excited molecules of nitrogen find themselves in the B_{10}, B_{11} and B_{12} states. The strong afterglow bands correspond to B-A transitions in which the vibrational quantum numbers change by -3, -4, -5 and -6. Because of the prevalence of these excited states the transitions B_{12}-A_{10} and B_{11}-A_9 might well be expected to appear in the afterglow. Therefore, the first heads of these bands were calculated and predicted to fall at 6670 Å and 6764 Å, respectively. From these predicted positions of the first heads, still using data presented by Poetker, it was possible to predict the second heads of these bands and these were found to be at 6754 Å and 6657 Å. On reëxamining the plates it was found that there was a single head at about 6750 Å superposed on a background of other normal first positive bands. This value, taken in conjunction with the position of the red "line," justifies the conclusion that these two single heads must correspond to the second heads of the bands arising from the B_{12}-A_{10} and the B_{11}-A_9 transitions. The meaning of the curtailed development of these bands as contrasted with the normal development of the other bands is not understood at present and this will be studied at the first opportunity. Because of the assignment of the "line" at 6654.8 to the α-group one can conclude definitely that the green line is the only line of oxygen that is excited by active nitrogen in the visible. This agrees with the bulk of experimental evidence according to which the green line is the only oxygen line that has been found in the Aurora Borealis and in the light of the night sky.

Recently McLennan, McLeod and Ruedy[3] concluded from the newly determined Zeemann effect of the green line, that it arises in a transition between the two low-lying metastable states $^1S_0$-$^1D_2$. Assuming this as the proper classification of the green line, one can give a lower limit to the wave-length of transitions between these two metastable states and the normal triplet levels $^3P_{0,1,2}$. This is done by simply remembering Hopfield's discovery that the energy difference between the two far ultraviolet singlet lines of oxygen at about 1217 and 999 A.U., respectively,

is exactly the energy corresponding to the green line. This means that the two lines correspond to transitions between a common upper level and the two metastable states, $^1S_0$ and $^1D_2$. This common upper level must therefore lie 12.34 volts above the $^1D_2$ level. Since the ionization potential of oxygen is 13.56 volts the transition $^1D_2$-$^3P_{0,1,2}$ can be no greater than 13.56 − 12.34 = 1.22 volts. Consequently, lines corresponding to those transitions must lie above 1μ. These are the only transitions that can result in a red auroral line and one is therefore not surprised at the non-observance of a red auroral line in the aurora or in the night sky.

Similarly, the transitions $^1S_0$-$^3P_{0,1,2}$ must lie at wave-lengths higher than 3575 A.U. and no such transitions have been observed in the Aurora, in the night sky or in laboratory experiments. This is not surprising because of the great improbability of intercombinations. It therefore seems probable that the green line is the only oxygen line in the auroral spectrum.

[1] *Nature*, **121**, p. 711, 1928.
[2] Poetker, *Phys. Rev.*, **30**, p. 812, 1927.
[3] McLennan, McLeod and Ruedy, *Phil. Mag.*, **6**, p. 558, 1928.

A VISUAL METHOD OF OBSERVING THE INFLUENCE OF ATMOSPHERIC CONDITIONS ON RADIO RECEPTION[1]

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There seems to be little doubt that radio signals may pass from one station to another by at least two different paths. The "ground wave" presumably follows the surface of the earth in much the same way that shorter waves are known to follow a wire. The "sky wave" starts obliquely upward from the sending station and reaches the observer after being bent or reflected by the Kennelly-Heaviside layer of highly ionized air. Both are subject to absorption due to the conductivity of the air, and the sky wave may have its plane of polarization rotated, or may suffer a sort of magnetic double refraction, because of the earth's magnetic field.

Changes in the ionization of the air and the height of the Heaviside layer will thus lead to changes in the amplitude, phase and polarization of the two waves, so that when both reach the receiving station together very complicated results are to be expected. That the results are in fact complicated and confusing is evidenced by the fading observed in broadcast reception and by the erratic changes in the apparent direction

of the waves as indicated by a radio compass. Since it is in the region of the Heaviside layer that the aurora occurs, and since there are strong reasons for believing that electric currents in this region have an important influence on the earth's magnetic field, the study of the effect of atmospheric conditions on radio reception is of importance, not only as a step toward improvement in methods of radio communication but also as one of the very small number of methods known to us by which we may hope to find out what the conditions in the upper atmosphere really are and thus obtain a check on theories of the aurora and of terrestrial magnetism.

Since it is the sky wave that is most influenced by atmospheric conditions some method of observation that will permit the effects of the sky wave alone to be measured is much to be desired. In the methods that are ordinarily used in studying radio reception the effect observed is always that due to the resultant of the two waves. Fading records, for example, if made with a vertical antenna, show the variation from instant to instant of the vertical component of the electric field at the receiving station, and this is due partly to the ground wave and partly to the sky wave. Direction settings made by a vertical loop receiver depend upon the direction of the *resultant* magnetic field. Thus far no means of completely separating the two waves has been proposed. In fact, complete separation does not seem possible.

In the experiments described in this paper a partial separation of the ground and sky waves is effected by the use of two carefully balanced coil receivers, one coil (A) being mounted with its plane vertical and directed toward the sending station, while the other (B) is set in the vertical plane at right angles to this direction. The response of the coil A is determined by the magnetic field due to the combined action of the ground wave and the vertically polarized component of the sky wave. The coil (B) is capable of receiving a signal only in case the resultant magnetic vector has a component directed toward the sending station; and this can occur only when waves reach the receiver which are moving in a direction having a downward component, and so polarized that the magnetic vector has a component in the vertical plane. This coil, therefore, responds only to that component of the sky wave which is polarized with its electrical vector horizontal. It is not affected at all by the ground wave.

To make possible convenient visual observation the signal received by the loop A was heterodyned by coupling to the circuit of a local oscillator, and after detection and suitable amplification was brought through a transformer to one pair of plates of a cathode ray oscilloscope, so as to produce a movement of the spot in the horizontal plane. Similarly the signal from loop B, heterodyned by the same local oscillator, was brought to the other pair of plates and caused a movement of the spot in the

vertical direction. The combination of the two movements resulted in a Lissajous figure on the oscilloscope screen.

Since the e.m.f. produced in the receiving circuit by the local oscillator is always greater than that due to either signal, the amplitudes of the vertical and horizontal oscillations of the oscilloscope are proportional to the amplitudes of the signals received by the two loops. And since the same local oscillator is used for heterodyning both signals, the phase difference between the vertical and horizontal oscillations is the same as that between the original signals. Thus if the signal received in A is $a \cos pt$ while that in B is $b \cos (pt + \varphi)$ the result of heterodyning with an e.m.f. $c \cos nt$ ($c > a$, and $c > b$) is to give for the circuit of loop A

$$a \cos pt + c \cos nt = (c - a)\cos nt + 2a \cos {}^1/_2(p - n)t \cos {}^1/_2(p + n)t$$

and for the circuit of loop B:

$$b \cos (pt + \varphi) + c \cos nt = (c - b)\cos nt + 2b \cos \left[\frac{1}{2}(p - n)t + \frac{\varphi}{2}\right] \cos \left[\frac{1}{2}(p + n)t + \frac{\varphi}{2}\right].$$

The complete cycle of amplitude change that is represented by the factor $\cos {}^1/_2(p - n)t$ contains two beats, so that the frequency of the beat tone after rectification by the detector tube is not ${}^1/_2(p - n)$ but $p - n$. Rectification produces no change, however, in the actual time shift between the beats from A and B, so that the phase shift *of the beat tone* is not $\varphi/2$ but φ; i.e., the same as the phase difference between the original signals.[2]

Thus the vertical and horizontal movements of the spot of light on the screen of the oscilloscope correspond both in amplitude and phase with the oscillations received by the two loops. The method would fail in the case of excessively rapid changes in the amplitude or phase of the waves. But there is no indication that such changes occur.

Thus far the method has been used chiefly with the carrier waves of a number of different broadcasting stations and gives a graphical picture of the changing phenomena that is both instructive and fascinating. It is surprising to find that modulation, unless unusually strong, is hardly noticeable and is rarely a source of disturbance.

Since the use of two loops at right angles gives only a partial separation of the ground and sky waves some caution must be used in interpreting the observed figures. Thus while there can be no vertical amplitude unless there is a sky wave, the absence of vertical amplitude does not necessarily mean that no sky wave is present, for it might be polarized with its electric vector in the vertical plane so as to produce no effect in loop B. In such cases the figure is a horizontal straight line, often changing slowly in length because of changes in the phase of the two waves.

During the day time the figure is usually a horizontal straight line of constant or very slowly changing length. As sunset approaches indications of a sky wave begin to appear. The line slowly pulsates, or tilts slowly back and forth about the horizontal. In other cases it opens up into a narrow ellipse which changes in area and inclination. On several occasions, about ten or fifteen minutes after sunset, the figure has been observed to rotate continuously—sometimes quite rapidly—in the same sense, changing at the same time from a line to an ellipse and back again. As many as twenty complete turns have been counted in a period of a few minutes. It seems not unlikely that this effect is due to the rapid rise of the Heaviside layer as darkness sets in. Due to the increasing length of path this would bring about a progressive change in phase of the sky wave, and at the same time a progressive rotation of its plane of polarization.

When a strong sky wave is present during the day time—and in the late afternoon this is not unusual—our observations thus far indicate that its modulation is much less marked than that of the ground wave. At night both waves appear to be modulated equally.

When night conditions have become established the movements of the figure are usually quite erratic. The vertical amplitude is often several times as great as the horizontal and both change rapidly. If rotation occurs it is sometimes in one direction and sometimes in the other. But although the changes are usually more rapid at night this is by no means always the case. We have observed circular polarization—indicated by a circular figure on the screen—which persisted with unchanged amplitude for as long as two minutes.

On Sept. 8, 1928, we were fortunate in being able to make visual observations during an auroral display. For several days before this date the conditions for radio reception had been unfavorable. The usual sunset phenomena were not observed and what we had come to regard as the normal night conditions were not established until quite late—if at all. On Sept. 8 observations were begun on station WEAF (New York) at 4:45 and at first indicated that conditions were still unfavorable. Only slight indications of a sky wave were observed and the changes in the oscilloscope figure were slow and not at all marked. The same conditions were found in the case of station WJZ (Bound Brook) and WGY (Schenectady) and continued with all three stations until 7:40, i.e., until more than an hour after sunset. The oscilloscope figure then began to change with great rapidity both in size and shape. During the greater part of this period of violent disturbance, which lasted until 7:48, the figure rotated counter clockwise, although the rotation was not at a uniform rate and was much confused by erratic changes. Then after a quiet period of about five minutes there was a slow clockwise rotation for over two

minutes. During the evening there were several other periods of continuous rotation sometimes in one sense and sometimes in the other. At 8:45 we shifted to station WGY (Schenectady) and found that the oscilloscope figure changed so rapidly that it could hardly be observed at all. Our first thought was that something had happened to the receiving sets and we devoted some time to adjusting and testing the apparatus, finding however that everything was in order. We then shifted to other stations and found that they were now showing just as violent and erratic changes as WGY. In the course of these adjustments and changes we noticed that a brilliant auroral display was in progress. Unfortunately, we have not been able to learn the hour at which the display began. The disturbed conditions persisted for about two hours, getting less marked as the aurora became fainter. At 11:10 conditions were normal and the aurora had disappeared.

The records of the Cheltenham Magnetic Observatory indicate a magnetic storm beginning at 1:48 P.M. Sept. 8 and ending at 9:30 P.M.

We have recently built two identical short wave sets and, although systematic observations have not yet been begun, have tested the method on a sufficient number of stations on this continent and in Europe to show that it can be used successfully with short waves as well as in the broadcast band. The oscilloscope figures are similar in character and movement to those observed with longer waves but usually change more rapidly. In the case of code stations we had rather expected that the interruption of the wave would prove a source of annoyance. We find however that the figure persists from one dash or dot to the next, while the absence of modulation results in a figure that is particularly sharp and clear.

It is our intention to continue observations, especially during the sunset period, both with signals from broadcasting stations in this country and with short wave from more distant stations.

[1] The investigation of which the work described in this paper forms a part has been supported by a grant from the Heckscher Foundation for Research at Cornell University.

[2] This method of determining the phase difference between two waves by observing the phase difference between the corresponding beat tones was developed by one of the writers in 1918 at the Naval Experimental Station, New London, the main purpose then being to make possible an adaptation of "binaural" methods of direction finding to radio signals. With other devices developed during the war by members of the scientific staff the method was later patented. (U. S. Patent No. 1,510,792, "Methods and Means for Determining Phase Difference," issued to Ernest Merritt.) In the original description of the method the phase difference between the beat tones is incorrectly given as $\varphi/2$. The procedure used by the authors to make the method a visual one has been used by H. T. Friis with the signals received by two similar vertical antennae spaced about one-third of a wave-length apart, and has led to an interesting modification of the binaural method in which phase differences are observed by the eye instead of by the ear. (H. T. Friis, "Direction of Propagation and Fading of Short Waves," *Proc. Inst. Radio Engineers*, **16**, p. 658, May, 1928.)

ON THE ENERGY OF DEFORMATION OF AN ELASTIC SOLID

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In the theory of elasticity as at present accepted[1] it is assumed that the energy of deformation is a function of the strain components and the various types of crystalline media are distinguished from one another and from an isotropic medium by the form of this function. It is the object of the present note to show that the mere assumption that the energy of deformation is a function of the strain components implies that it is a function of the three strain invariants so that the medium is necessarily isotropic elastically. For a crystalline medium, therefore, it is impossible that the energy of deformation can be a function of the strain components alone; it will involve, probably, the space rates of change of these components.

If the initial and final rectangular Cartesian coördinates of a particle of the medium be denoted by (x_0, y_0, z_0) and (x, y, z), respectively, it follows that $ds^2 - ds_0^2 = 2[E_1dx^2 + E_2dy^2 + E_3dz^2 + 2E_4dydz + 2E_5dzdx + 2E_6dxdy]$, where if $U = x - x_0$, $V = y - y_0$, $W = z - z_0$ denote the displacement components, $E_1 = \frac{\partial U}{\partial x} - \frac{1}{2}\left[\left(\frac{\partial U}{\partial x}\right)^2 + \left(\frac{\partial V}{\partial x}\right)^2 + \left(\frac{\partial W}{\partial x}\right)^2\right]$, with similar expressions for E_2 and E_3, and $E_4 = \frac{1}{2}\left(\frac{\partial W}{\partial y} + \frac{\partial V}{\partial z}\right) - \frac{1}{2}\left[\frac{\partial U}{\partial y}\frac{\partial U}{\partial z} + \frac{\partial V}{\partial y}\frac{\partial V}{\partial z} + \frac{\partial W}{\partial y}\frac{\partial W}{\partial z}\right]$, with similar expressions for E_5 and E_6. The six quantities $E_1, \ldots\ldots E_6$ are known as the strain components and they reduce, for an infinitesimal deformation, to the simpler expressions $E_1 = \frac{\partial U}{\partial x}$, etc; $E_4 = \frac{1}{2}\left(\frac{\partial W}{\partial y} + \frac{\partial V}{\partial z}\right)$; etc. Now in order to use the energy principle we must consider not only the initial and final positions (x_0, y_0, z_0) and (x, y, z) of any particle but also the continuous sequence of positions between these two. In other words, the coördinates (x, y, z) must be thought of as functions of (x_0, y_0, z_0) and of a parameter θ, which might conveniently be the time. It is easily shown[2] that the virtual work of the various forces, both mass and surface, acting on the medium is given by the volume integral

$$\int \left\{ X_x \frac{\partial}{\partial x}\delta U + Y_y \frac{\partial}{\partial y}\delta V + Z_z \frac{\partial}{\partial z}\delta W + Y_z\left(\frac{\partial}{\partial y}\delta W + \frac{\partial}{\partial z}\delta V\right) + Z_x\left(\frac{\partial}{\partial z}\delta U + \frac{\partial}{\partial x}\delta W\right) + X_y\left(\frac{\partial}{\partial x}\delta V + \frac{\partial}{\partial y}\delta U\right) \right\} d\tau$$

where $(X_x, Y_y, Z_z, Y_z, Z_x, X_y)$ denote the components of the symmetrical

stress tensor and where δU, for example, denotes $\frac{\delta U}{\delta\theta}\,d\theta$, U being regarded as a function of x_0, y_0, z_0 and θ. It is essential to notice that, while the variables x_0, y_0, z_0 and θ are, by hypothesis, independent, the variables x, y, z and θ are not; thus it is not allowable to interchange the order of differentiation with respect to x and θ, for example, and to write $\frac{\partial}{\partial x}\delta U = \delta\frac{\partial U}{\partial x}$. We have, in fact, $\delta U = \frac{\partial U}{\partial x}\delta x + \frac{\partial U}{\partial y}\delta y + \frac{\partial U}{\partial z}\delta z + \frac{\partial U}{\partial\theta}\delta\theta = \frac{\partial U}{\partial x}\delta U + \frac{\partial U}{\partial y}\delta V + \frac{\partial U}{\partial z}\delta W + \frac{\partial U}{\partial\theta}\delta\theta$ where U is regarded as a function of x, y, z and θ, and proceeding in this way we have the system of linear equations

$$\sum_{a=1}^{3} f_{ra}\frac{\partial}{\partial x^s}\delta U_a = \delta\frac{\partial U_r}{\partial x^s}.$$

In writing these equations (U, V, W) and (x, y, z) have been replaced, for convenience by (U_1, U_2, U_3) and (x^1, x^2, x^3), respectively, and $f_{rs} = \delta^r_s - \frac{\partial U_r}{\partial x^s}$ where $\delta^r_s = 1$ or 0 according as $r =$ or $\neq s$. On solving these linear equations for $\frac{\partial}{\partial x^s}\delta U_r$ and substituting in the expression for the virtual work this appears as the integral of a linear form in the differentials $\delta\frac{\partial U_r}{\partial x^s}$. The energy principle tells us to equate the virtual work to the integral $\int\delta\phi\,.d\tau$ where φ is the energy of deformation and since the partial derivatives $\frac{\partial U_r}{\partial x^s}$ are independent quantities we may, on the assumption that ϕ is a function of these partial derivatives, equate the coefficient of $\delta\frac{\partial U_r}{\partial x^s}$ in the integrand of the virtual work integral to $\frac{\partial\varphi}{\partial\left(\frac{\partial U_r}{\partial x^s}\right)}$. If we further assume that φ involves the nine partial derivatives $\frac{\partial U_r}{\partial x^s}$ only through the six strain components $(E_1, \ldots\ldots E_6)$ we are led to the results

$$X_x = \frac{\partial\varphi}{\partial E_1} - \left(2E_1\frac{\partial\varphi}{\partial E_1} + E_5\frac{\partial\varphi}{\partial E_5} + E_6\frac{\partial\varphi}{\partial E_6}\right)$$

$$Y_z = \frac{1}{2}\frac{\partial\varphi}{\partial E_4} - \left(2E_4\frac{\partial\varphi}{\partial E_2} + E_5\frac{\partial\varphi}{\partial E_6} + E_3\frac{\partial\varphi}{\partial E_4}\right);$$

$$Z_y = \frac{1}{2}\frac{\partial\varphi}{\partial E_4} - \left(2E_4\frac{\partial\varphi}{\partial E_3} + E_2\frac{\partial\varphi}{\partial E_4} + E_6\frac{\partial\varphi}{\partial E_5}\right)$$

and others obtainable from these by cyclic permutation of the two triads of labels (1,2,3) and (4,5,6). The classical results are given by the first terms in these expressions, namely,

$$X_x = \frac{\partial \varphi}{\partial E_1} \; ; \; \ldots \; Y_z = \frac{1}{2}\frac{\partial \varphi}{\partial E_4} = Z_y$$

and these may be obtained at once from the more general result by expanding φ in a Taylor series development in the E's, starting with quadratic terms and then treating $E_1, \ldots\ldots E_6$ as infinitesimals. However, *and this is the point of this note,* it is evident that the simplification due to the assumption that the strain is infinitesimal has been made too soon in the classical theory. For it has caused us to lose sight of the fact that the symmetry of the stress tensor gives us information about the nature of the function φ. Thus the equation $Y_z = Z_y$ yields

$$2E_4\frac{\partial \varphi}{\partial E_2} - 2E_4\frac{\partial \varphi}{\partial E_3} + (E_3 - E_2)\frac{\partial \varphi}{\partial E_4} - E_6\frac{\partial \varphi}{\partial E_5} + E_5\frac{\partial \varphi}{\partial E_6} = 0$$

and there are two similar equations obtainable by permuting cyclically the two triads of labels (1,2,3) and (4,5,6). It is immediately verifiable that these three linear homogeneous partial differential equations of the first order possess the three common and distinct solutions

$$I_1 = E_1 + E_2 + E_3; \; I_2 = (E_2E_3 - E_4^2) + (E_3E_1 - E_5^2) + (E_1E_2 - E_6^2); \; I_3 = \begin{vmatrix} E_1 & E_6 & E_5 \\ E_6 & E_2 & E_4 \\ E_5 & E_4 & E_3 \end{vmatrix}$$

and since there are six variables $(E_1, \ldots\ldots E_6)$ we know that the general solution must be a function of these three particular solutions. Hence φ must be a function of the three strain invariants I_1, I_2, I_3 and the medium must be elastically isotropic.

Attention may be directed to the fact that our result has been obtained without making any assumption that the deformation is infinitesimal. For a detailed exposition we may refer to the forthcoming 1929 volume of the *American Journal of Mathematics.*

[1] Love, A. E. H., *The Mathematical Theory of Elasticity,* 3rd Edition, Chapters 3 and 6.

[2] Love, loc. cit., p. 92.

THE SURVIVAL OF INTELLIGENCE

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The ordinary method of estimating the fertility of the stocks which produced any group by ascertaining the number of its siblings may be extended by the inclusion of cousins. An inquiry of this sort was conducted recently by means of a printed questionnaire presented to the entire membership of Clark University, 31 controls from the city of Worcester (mostly nurses in training) and about a dozen faculty members from Cornell University. The question (excluding explanatory matter) took the form: "How many grandchildren did each of your grandparents have? Count each child born alive, and include yourself." It was answered by a total of 216 persons, two of the returns being incomplete.

The results take the form of four values for each individual, one for each of his grandparents. It is necessary to derive an index which shall combine these values in such a way as to show the number of individuals or equivalents of individuals in the propositus generation representing the four individuals of the grandparental generation. It may be observed at once that the propositus and his siblings represent the grandparents completely, being descended from them and from nobody else in their generation. Half-siblings and cousins, however, are descended in part from the grandparents in question, and in part from two other grandparents. The appropriate index, therefore, may be secured by adding to the number in the propositus' immediate family half the number of half-siblings and cousins; this, however, turns out to be the simple average of the four values, and this may, then, be referred to as the *survival index*. It is evident that, barring juvenile mortality, a survival index of 4.0 would be sufficient to maintain a stock; since, however, mortality by the age of 27 (which we may take as a reasonable reproductive age) is 25%, we may take 5.3 as the appropriate maintenance value. The following are the percentages falling below 6.0 for the group studied, by subgroups:

	%	N
Faculty	20	46
Graduates	17	42
Seniors	17	12
Juniors	26	23
Sophomores	39	31
Freshmen	38	29
Controls	26	31
Average	26	214

The following distribution gives the major characteristics of the total group:

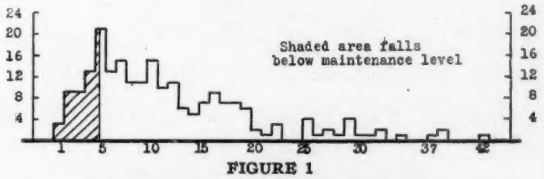

FIGURE 1

Frequency of survival index, all subjects.

The comparison of the subgroups may be undertaken either by means, or, since the distributions are markedly skewed, by medians; there is an absolute difference of about two and a quarter points, but the relative difference is slight:

	M	σ_M	Md	σ_{Md}
Faculty	11.2	0.98	9.2	1.0
Graduates	14.7	1.20	13.0	1.6
Seniors	13.3	2.13	9.7	1.2
Juniors	11.9	1.36	10.0	2.4
Sophomores	10.0	1.00	7.5	1.2
Freshmen	10.9	1.20	8.5	2.0
Controls	10.9	1.09	9.0	1.2

Figure 2 presents the same facts graphically:

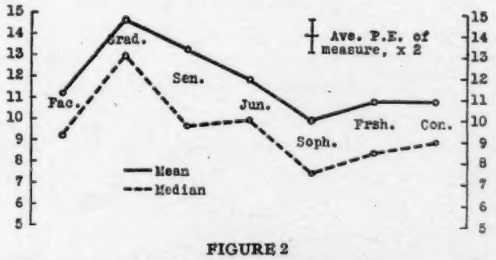

FIGURE 2

Survival index averages, by groups.

The evidence seems clear that there is a fairly reliable decline in the survival index as we go from more intelligent to less intelligent groups of the population. This is not the case, however. For 60 undergraduates, 9 graduates and 2 faculty we have intelligence test scores warranting their assignment to a percentile in a distribution of college students; correlating these percentiles with the survival indices yields an r of -0.28 ± 0.07, which is increased to -0.32 ± 0.08 by dropping out the faculty and graduates, all but two of whom are in the top 1 or 2% in intelligence; analysis by classes shows the same tendency in seniors, juniors and fresh-

men, with sophomores indeterminate. The following table shows that (with the exception of the sophomores) the undergraduates for whom we have intelligence data (Column *A*) are a representative fraction of those for whom we have survival indices (Column *B*), but that judged by their median percentile (Column *C*) they are not an unselected group of college students:

	A	*B*	*C*
Seniors	8	12	60
Juniors	20	23	42
Sophomores	7	31	50
Freshmen	25	29	74

Instead of the decline in the survival index accompanying a decrease in the intelligence of the groups, then, it accompanies an *increase*, and the negative tendency indicated by the correlation is confirmed—partly. The modifier is necessary because by taking three variables in each of two phases (intelligence increasing and decreasing, index increasing or decreasing, correlation positive or negative) eight diagrams may be drawn demonstrating the possibility of any phase of one coexisting with any phase of either of the others.

In summary, by an extension of the sibling method of determining the fertility of stocks backward one more generation, and its application to 214 college men and controls, a relation between fertility and intelligence indicated by an r of -0.3 has been shown; a marked drop in average survival from the older to the younger academic groups (faculty excluded), appearing to indicate a positive relation, is probably due to a local reversal of the expected principle of selection. There are no marked differences between the controls and the lower academic groups, and the faculty group is also not conspicuously different from these. The point deserves emphasis that in none of the groups studied are the stocks on the average anywhere near the level at which continued maintenance is menaced, the average proportion falling below a liberal estimate of that level being only about one-quarter.

ACKNOWLEDGMENT

The problem treated in the article "A Case of Streaming in a Valve" in the April issue of the PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES, was indicated to me by Professor Blumenthal of Aachen (Germany) who had already found the results contained in the article, and proposed to me to develop the subject further. Guided by his advice, I refound the results. I regret that, through a misunderstanding, they were offered in my behalf to the PROCEEDINGS.

E. BODEWIG